

# Modeling and Simulation of the Algae to Biodiesel Fuel Cycle

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# Chapter 1

## Introduction

### *1.1 Motivation*

Transportation is the lynch pin of our society, powering the economies of the world everyday. Petroleum based fuels account for 97% of transportation energy, without petroleum food and products could not be shipped from place to place, people could not drive to work, and the world as we know it will no longer exist. At our staggering consumption levels the worlds petroleum reserves will be exhausted in the next 30 to 40 years. To compound this problem the existing petroleum powered transportation network is responsible for a large amount of the hazardous emissions causing global warming and air pollution problems worldwide. A viable energy source that eliminates petroleum and reduces green house gas emissions must be found.

In 2004 the United States consumed over 7.5 billion barrels of oil and 24% of this was in the form of diesel fuel, which is the driving force behind the trucking and shipping industry (U.S. Energy Information Administration EIA). In the U.S. last year these activities resulted in the consumption of over 64 billion gallons of diesel fuel. At these staggering consumption rates, which increase every year, the limited world petroleum



reserves are only expected to last another 30 years according to the United States Energy Information Administration (EIA). Figure 1.1 displayed below shows the dramatic drop off in petroleum supply that is forecast in the year 2030.

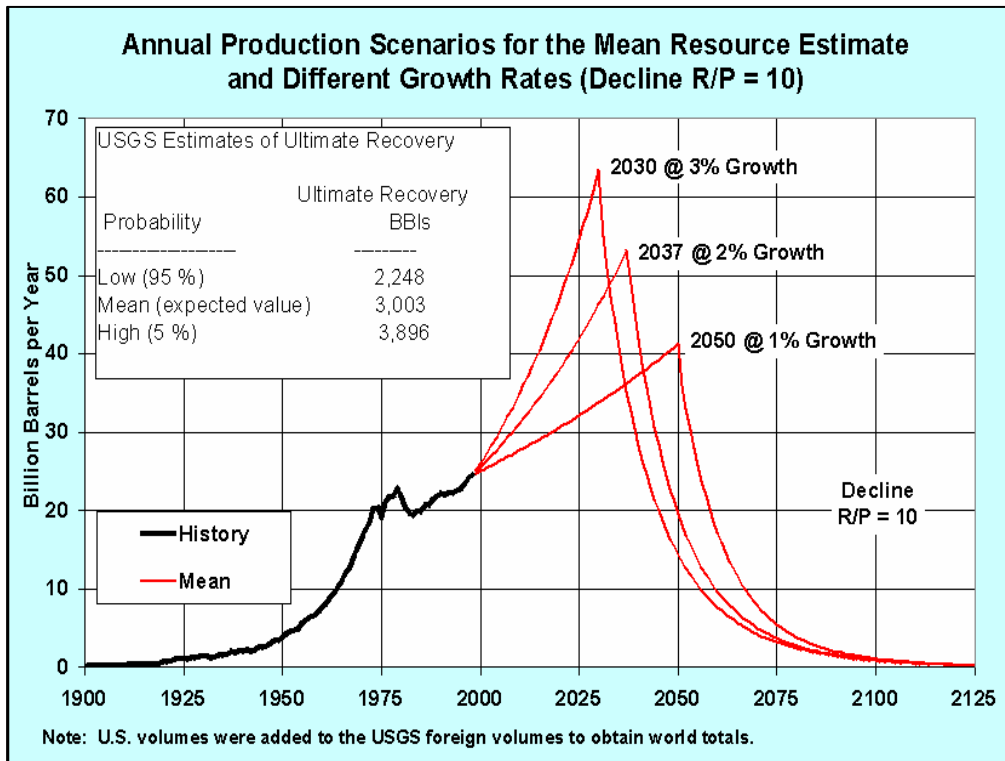


Figure 1.1: Petroleum forecast

Many experts around the world feel that this is a very generous assumption. For example Dr. Seppo Korpela a professor in mechanical engineering at Ohio State University has extensively studied the phenomena of peak oil and he claims that we will reach peak oil production within the next 10 years.

Everyday hazardous emissions are dumped into the atmosphere, 25% of green house gases in the United States result from the transportation sector (EIA). These emissions are causing worldwide global warming and air pollution problems. Smog that fills cities around the world is generated from the cars and trucks that swarm the streets.

These are becoming major problems in the U.S. and the world, with the transportation industry being one of the main contributors to these problems.

An alternative form of energy that reduces petroleum consumption and cuts down on hazardous emissions must emerge to power the transportation network. There are many organizations and companies are searching for viable alternatives. To compare these various alternatives Argonne National Labs created the Green house gases Regulated Emissions and Energy use in Transportation (GREET) model. The GREET model analyzes the well-to-wheel energy use and emissions resulting from the various fuel cycles and compares them to the current petroleum fuel cycle. After extensively analyzing GREET model results I decided to conduct a more in depth study of biodiesel.

Biodiesel is a proven technology and a very attractive alternative fuel source. It can be made from any fat or vegetable oil, currently the majority of biodiesel produced in the U.S. comes from soybeans. This current system provides an energy benefit of 35% meaning that you are left with 35% more energy then is put into the system. It provides a substantial reduction in green house gases, and can be used in current diesel vehicles with minor modifications. The major drawback of biodiesel is that only 42 gallons of biodiesel are produced on an acre of farm land. Even if all of the soybeans grown in the U.S. were used for biodiesel production, it would be well short of or current diesel consumption. A new higher yielding source of biodiesel must be discovered in order to justify biodiesel the source to power our transportation needs.

Microalgae are remarkably efficient biological factories capable of taking a waste (zero-energy) form of carbon (CO<sub>2</sub>) and converting it into natural oil. Microalgae have

been found to have incredible production levels compared to other oil seed crops like soybeans. Table 1.1 below shows a comparison of oil yield for various oilseed crops.

Production Averages for Common Oil Crops		
Plant	lb. oil/acre	Gallons of biodiesel/acre
Algae	6,757	700
Coconut	2,070	285
Jatropha	1,460	201
Rapeseed	915	126
Peanut	815	112
Sunflower	720	99
Soybean	450	62

**Table 1.1: Production averages for common oil crops**

Extensive research has been carried out to develop high rate algae growth systems capable of producing biodiesel on a large scale. The United States Department of Energy (DOE) carried out an 18 year study of biodiesel production from algae, and this study is discussed in detail in Chapter 2. For my honors research project I developed a model that predicts the production levels as well as the energy use and emissions of the algae farms placed at various locations throughout the United States.

The following chapters discuss in detail the research that I conducted on the algae to biodiesel fuel cycle and the GREET model. Chapter 4 describes the Algae Pond Model and how it was created. The results obtained from modeling the algae to biodiesel fuel cycle are discussed in chapter 5, and conclusions and recommendations are given in Chapter 6.

## **Chapter 2**

### **Literature Review**

#### ***2.1 The Aquatic Species Program***

This chapter analyzes each step of the algae to biodiesel process, and begins with a review of previous algae to biodiesel studies. From 1978 to 1996, the United States Department of Energy's Office of Fuels Development funded the Aquatic Species Program (ASP). The focus of the program was to develop renewable transportation fuels from algae. Extensive research was conducted on the production of biodiesel from algae grown in large raceway ponds that use waste CO<sub>2</sub> from coal fired power plants as a fertilizer for the algae. The main highlights of the program are described in the following sections.

##### ***2.1.1 Algae Classification***

The study began by trying to determine which species of algae would be suitable for the purpose of developing transportation fuels. For the production of biodiesel the selected strain of algae must have very high growth rates and a very high lipid or oil

content. There are well over 100,000 different species of algae, so the scientists involved in the study had the daunting task of analyzing these species and determining which were most suitable for producing biodiesel. By the end of the study the researchers had identified around 300 strains of algae that are the most suitable for producing biodiesel. They all have high growth rates, oil content, and are capable of growing in harsh climates. These strains of algae are currently housed at the University of Hawaii, and are available to interested researchers (Benemann, 1996).

### ***2.1.2 Biochemistry and Molecular Biology***

Next researchers focused their efforts on using biochemistry to manipulate the algae to have higher oil content. The goal of this research was to take advantage of the “lipid trigger”, which is the phenomenon that occurs when microalgae are under environmental stress many species go through a metamorphosis and begin producing very large amounts of oil (Benemann, 1996). Researchers thought that this could be done by denying the algae certain nutrients, specifically nitrogen. However in the end the researchers concluded that although the nitrogen deficiency did increase the oil content of the algae it does not lead to increased oil productivity because it reduces the growth rates of the algae.

During this time researchers were also attempting to genetically modify the certain algae species so that they would produce more oil and also enable them to grow in very harsh environments. Although the researchers did make significant discoveries they were unable to demonstrate increased oil production in the cells. Researchers concluded

that for future endeavors strains of algae should be selected that are native to the region where commercial microalgae production sites are planned.

### ***2.1.3 Algae Production Systems***

Over the course of the program several test sites were constructed to examine the feasibility of large scale algae production in open ponds. Many different algae growth systems have been studied, for example the Japanese government have developed optical fiber based reactor systems that could dramatically reduce the amount of surface area required for algae production. However while breakthroughs in these types of systems have occurred their costs are prohibitive, especially for the production of fuels. The ASP focused on open pond raceway systems because of their relative low cost (Benemann, 1996). The Algae Pond Model, which is a program developed in Matlab to predict the energy use and emissions that result from growing algae in various regions, is based off of the results obtain during the operation of the Microalgae Outdoor Test Facility (OTF) in Roswell, New Mexico.

### **2.1.4 Microalgae Outdoor Test Facility (OTF)**

In 1987 construction began on an algae growth facility consisting of two 1,000m<sup>2</sup> ponds, one plastic lined and another unlined, and six small, 3m<sup>2</sup> ponds. An abandon water research facility in Roswell New Mexico was the site chosen for this operation. Roswell receives large amounts of daily solar radiation and has abundant flat desert land with large supplies of saline groundwater, making it an excellent location for algae growth. One limitation of the site was the low nightly temperatures, which turned out to be to low for many of the more productive species identified.

Building the large system required installation of two water pipeline of 1,300m in length. The ponds were 14 x 77 m, with concrete block walls and a central wooden divider. The paddle wheels were approximately 5m wide, with a sump that allowed counter flow injection of CO<sub>2</sub>. One pond was plastic lined; the other had a crushed rock layer, and the walls were cinder block (Benemann, 1996). Figure 2.1 below shows an overview of the layout of the facility.

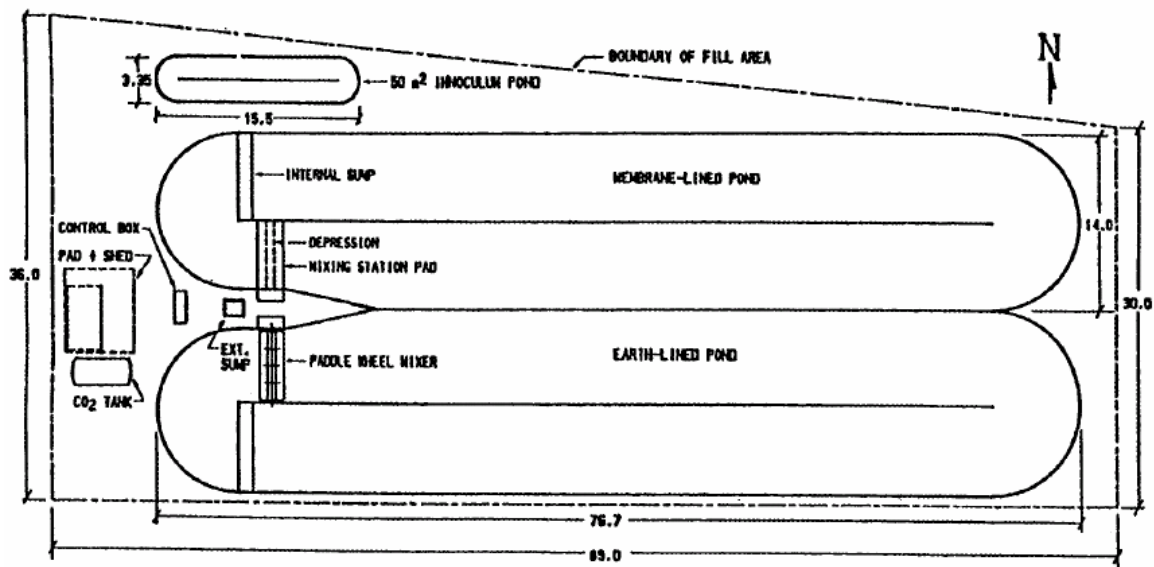


Figure 2.1: Schematic of microalgae OTF facility in Roswell, New Mexico

The OTF facility experimented with three different species of algae; first they used *C. cryptica* CYCLO1. *C. cryptica* had high productivities in the summer months but reaching 30 g/m<sup>2</sup>/d but fell off drastically during when the weather became colder. Next *M. minutum* (MONOR2) a more cold-tolerant organism was used. Even though productivity in the winter was very low 3.5 g/m<sup>2</sup>/d in December the algae survived despite the ponds freezing over multiple times. Next *Amphora* sp. was used and although it exhibited growth rates above 40 g/m<sup>2</sup>/d in the summer it also could not survive in the

winter months. Because of its survivability *M. minutum* was selected as the most suitable strain of algae for the Roswell location (Goebel, 1989).

The OTF facility operated the large scale ponds for two years, by the end of the study they had determined some important parameters for future algae ponds:

- 1) Power for pond mixing is quite low around 0.1 kW/1,000m<sup>2</sup> pond.
- 2) Pond mixing should be in the 15-25 cm/s range, and pond depth 15-25 cm.
- 3) CO<sub>2</sub> utilization efficiencies of near 90% overall should be achievable.
- 4) Large-scale pond productivities of 70 mt/ha/yr are realistic goals for this process.
- 5) The small-scale ponds can be used to screen strains and optimize conditions.

The results from the OTF large scale ponds are shown in table 2.1 below; the APM is based off of these results.

Pond Liner	CO <sub>2</sub> use (m <sup>2</sup> /d)	Dates	Productivity (gm afdw/m <sup>2</sup> /d)	Carbon Use Efficiency	Water Loss (mm/d)
YES	15.2	10/1/88 - 9/30/89	9.8	59	5.7
NO	13.4	10/1/88 - 9/30/89	8.3	50	6.2
NO	14.6	10/1/89 - 9/30/90	10.5	82	
YES	22.0	6/1/90 - 10/30/90	19	81	
NO	19.2	5/1/90 - 9/30/90	18	88	

**Table 2.1: Long Term OTF Results from 1,000 square meter Raceways**

Notes: gm/afdw/m<sup>2</sup>/d: grams of ash-free dry mass per square meter per day  
Pond liner: YES indicates a plastic lined pond; NO indicated dirt bottom

## ***2.2 Algae Growth in Outdoor Raceway Ponds***

This section is a step by step walk through of the algae to biodiesel process. The size of the algae ponds are 1,000m<sup>2</sup> the same size studied in the OTF. All of the processes discussed in this section are modeled in the Algae Pond Model. First the algae



pond operations are analyzed, followed by the oil extraction process, and finally transesterification or biodiesel production.

### **2.2.1 *Microalgae***

Micro algae are remarkably efficient biological factories capable of taking a waste (zero-energy) form of carbon (CO<sub>2</sub>) and converting it into a high density liquid form of energy (natural oil). The four most abundant classes of micro algae are diatoms (Bacillariophyceae), green algae (Chlorophyceae), blue-green algae (Cyanophyceae), and golden algae (Chrysophyceae). Diatoms were the only class of micro algae analyzed in this study. They are found in fresh and salt water, and they store carbon in the form of natural oils or as a polymer of carbohydrates. (Benemann, 1996)

For the algae to biodiesel cycle to be successful a species of algae that has high growth rates and oil content must be used. The Aquatic Species Program recommends that an effort be made to naturally select strains at the locations that would likely be commercial micro algal production sites. In this manner, the algae would be exposed to the prevailing environmental conditions, particularly the indigenous waters. If a non-native strain of algae is used it is likely that a native species will infiltrate the pond and over time dominate the pond, killing off the desired strain. The Algae Pond Model is based off of the results obtained at the OTF using a unicellular green algae called *Monoraphidium minutum* (M. minutum).

Algae reproduce by cellular division. They divide and divide and divide until they fill whatever space they are in or exhaust their nutrients (Tickell, 2003). There are multiple stages of algae growth that depend on the culture volume and algae density.

Assume there is a small batch of algae is placed into a large volume tank mixing tank, and that the tank is supplied with enough CO<sub>2</sub> and sunlight to generate maximum growth. Some form of agitation, such as shaking or mixing is necessary to ensure nutrient and gaseous exchange. The algae will initially enter an exponential growth phase, where cells grow and divide as an exponential function of time, as long as mineral substrates and light energy are saturated (Richmond, 2003). When the concentration of algae is high enough that light does not penetrate through the entire culture, the algae move into the light limited linear growth phase, which is expressed by the following equation (Richmond, 2003).

$$IA = u * X * V / Y$$

$I$  = Photon flux density ( $\text{h J m}^{-2}$ )<sup>-1</sup>

$A$  = Illuminated surface area ( $\text{m}^2$ )

$u$  = Specific growth rate ( $\text{h}^{-1}$ )

$X$  = Biomass concentration (grams/liter)

$V$  = Culture volume ( $\text{m}^3$ )

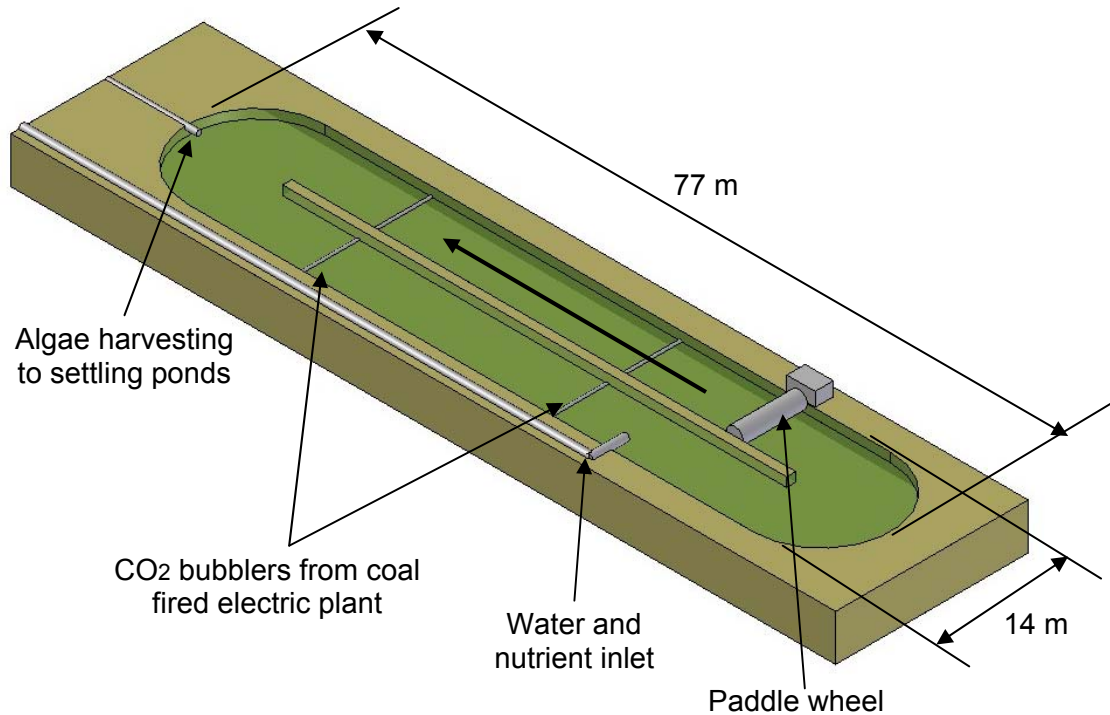
$Y$  = Growth yield (g/J)

Finally if the size of the tank is not increased the algae will eventually reach a terminal density and stop growing.

Algae growing in a flowing pond or raceway will operate in the light limited linear growth stage. The exponential growth stage is not achievable, since the algae are not all subject to the necessary amount of solar radiation. As algae cycle around the race way pond a certain percentage of algae will be harvest leaving the remaining algae room to grow in the linear growth range. Maintaining the algae in the linear growth range has allowed the model of algae growth to be controlled by linear relationships

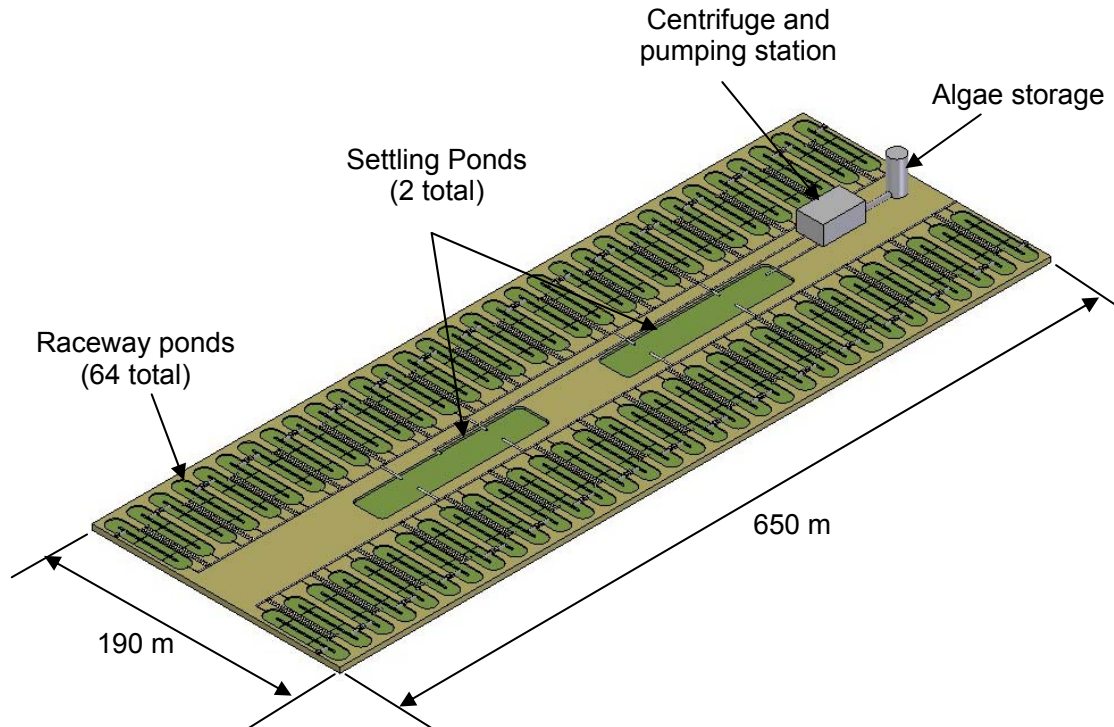
### 2.2.2 Algae Pond Operations

A scaled version of the 1,000m<sup>2</sup> algae pond is shown in figure 2.2 below.



**Figure 2.2: Scaled model of a 1,000 m<sup>2</sup> algae pond**

This is the pond that the APM is modeled after. The pond depth is 20 cm corresponding to a volume of 200 m<sup>3</sup> or 200,000 liters, it is unlined and powered entirely by electricity. Many ponds of this size would be fit into a small area along with larger settling ponds and a pumping centrifuge station in order to produce algae on a large scale. Figure 2.3 below is a scaled layout of what one of these facilities might look like.



**Figure 2.3: Scaled model of large algae farm for production of biodiesel**

Algae pond operations are very simple. The algae are introduced into the pond and allowed to grow until they occupy 1% of the volume of the pond. Very high growth rates are achieved because the pond is constantly mixed by the paddle wheel and it is infused with an ample amount of  $\text{CO}_2$  and fertilizer. The paddle wheel rotates providing a current of 20 cm/s around the pond. The mixing is required to ensure that all of the algae receive the necessary amounts of solar radiation,  $\text{CO}_2$ , and fertilizer required for optimal growth.

The  $\text{CO}_2$  is injected into the algae pond in the form of flume gas from a nearby coal fired electric plant. The bubblers are spaced around the pond so that the  $\text{CO}_2$  is evenly dispersed throughout the pond. A 1,000  $\text{m}^2$  algae pond operating in Roswell New Mexico consumes around 10,589 kg of  $\text{CO}_2$  each year. This is a miniscule amount

considering that the average 785 MW power plant produces 19,488 tons of CO<sub>2</sub> daily, or enough to support about 330,000 algae ponds (CleartheAir, 2000).

Algae require a certain amount of phosphorus and nitrogen to grow at optimal rates. The phosphorus and nitrogen are pumped into the ponds along with ground water from the central pumping station shown in figure 2.3. The nitrogen is in the form of ammonia or nitrate and must compose 0.8% of the volume of the pond solution to ensure maximum algae production. Likewise phosphorus is in the form of phosphate and must compose 0.6% of the pond (Benemann, 2006). In the future both of these nutrients could be supplied in the form of municipal solid waste. Water must also be continuously supplied to the ponds because a certain amount is lost daily due to evaporation and farm operations. The OTF tests recorded an average water loss of 6.2 mm or 6.2 m<sup>3</sup> of water per day. This must be replaced with saline or fresh ground water depending on the species of algae used.

### ***2.2.3 Algae Harvesting***

Algae harvesting is one of the major factors that must be overcome in order for algae to be used as a fuel source. The problem is that microalgae mass cultures are dilute, typically less than 500 mg/l on a dry weight organic basis, and the cells are very small. Many unicellular species like *M. minutum* are around 5 micrometers in diameter. In order to be processed into biodiesel the algae must be in the form of a paste that is 15% solids. In the raceway ponds the mixture is about 1% solids, this mixture must go through a process which will result in a concentration of at least 15%.

Many different algae harvesting processes have been studied figure 2.4 below shows a number of these processes which were studied by Dr. John Benemann in 1996.

<b>Process</b>	<b>Main Mechanism</b>	<b>Major Inputs</b>	<b>Dependence on algae</b>	<b>Relative Cost</b>	<b>Concent. Solids</b>	<b>Energy Inputs</b>
<b>Centrifugation</b>	Accelerated discrete settling	Power Equipment	minor	10	> 10%	high
<b>Chem. Flocculation</b>						
<b>Inorganic lime</b>	floc enmeshment	Lime + Mix.	minor	6 - 8	8 - 10%	high
<b>alumn</b>	" + destabilize	Alumn + Mix.	minor	6 - 8	8 - 10%	high
<b>Polyelectrolytes</b>	" + " + bridging	PE + Mixing	minor	4 - 6	8 - 10%	medium
<b>Cross Flow Filtration</b>	Membrane self cleaning	Power Equipment	minor	4 - 6	2 - 6%	high
<b>Microstraining</b>	fabric straining "Schmutzdecke"	Power Equipment	high	0.5 - 1.5	2 - 4%	medium
<b>High Grad. Mag. Sep.</b>	Adsorption of Magnetic Particle	Power Equipment	Unk.	Unk.	Unk.	Unk.
<b>Discrete Sedimentation</b>	Gravity Discrete Settling	Pumping, Clarifier	high	0.5 - 1	1 - 3%	low
<b>Bioflocculation</b>	Spontaneous Flocculation	Pumping, Clarifier	high	0.5 - 1	1 - 3%	low
<b>Autoflocculation</b>	Ca/Mg ppt. induced flocc	Pumping, Clarifier	minor	0.5 - 1	1 - 3%	low
<b>Autoconcentration</b>	Phototaxis	Pumping, Clarifier	high	Unk.	Unk.	low?

Figure 2.4: Comparative evaluation of harvesting processes

Centrifugation – The algae pond solution is pumped into a large centrifuge, which rotates at several thousand RPM causing the algae to be pressed against the outer wall, which is a filter only a few microns in spacing. The water is forced out, while the algae remain of the screen in the form of a paste about 20% algae. This is a proven method that has been extensively used when working with microalgae. Studies have determined that a nozzle disc type centrifuge with intermittent discharge is the best option for algae

harvesting (Mohn, 1988). The downfall however is the high power requirements or high cost associated with operating the centrifuge.

Chemical flocculation – Certain chemicals like lime, alum, or chitosan can be added to the algae pond solution causing charge neutralization of the algae. This results in the algae clumping together. There is also a very high cost associated with this method, because of the large amounts of chemicals that are required.

The APM uses settling ponds as the initial harvesting method, which will bring the solution to 3% algae. From the settling ponds this mixture will be put through a centrifuge which will bring the mixture to 15% algae. Using the settling ponds will help to reduce energy consumption and cost of centrifuge operations.

## ***2.3 Biodiesel Production***

In order to be converted into a liquid fuel the oil contained in the algae must be extracted. According to Nick Nagle a senior engineer at the NREL who was a vital part of the ASP, algae oil extraction is very similar to soybean oil extraction, and can be modeled the same. The oil is extracted by mixing Hexane, a chemical made from petroleum, with the algae paste. The hexane removes the oil from the algae, this mixture of hexane and oil is distilled leaving pure algae oil. The remaining hexane is recycled through another batch of algae. The algae fiber remaining after this process can be used as fertilizer for the algae farms.

### 2.3.2 Transesterification

Transesterification is the process that the algae oil must go through to become biodiesel. It is a simple chemical reaction requiring only four steps and two chemicals.

1. Mix methanol and sodium hydroxide creates sodium methoxide
2. Mix sodium methoxide into algae oil
3. Allow to settle for about 8 hours
4. Drain glycerin and filter biodiesel to 5 microns

Figure 2.5 below shows the inputs and outputs of this process.

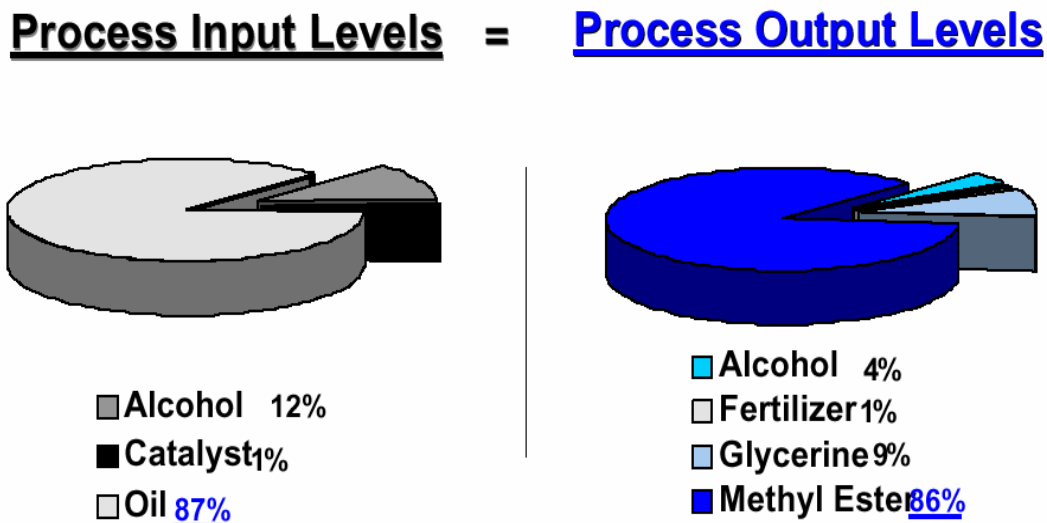


Figure 2.5: Inputs and outputs of transesterification reaction

The alcohol used in this reaction can be either methanol or ethanol, the catalyst is sodium hydroxide, and the oil is any fat or vegetable oil. The outputs are 86% Methyl Esters or biodiesel, 9% Glycerine which can be used to make soap and other products, 1% fertilizer, and 4% alcohol which can be recycled back through the process (Tickell, 2003).



## Chapter 3

# Methodology of the (GREET) Model

### *3.1 The GREET Model*

The Green house gases Regulated Emissions and Energy use in Transportation (GREET) model was created by Argonne National Laboratory. The model follows the entire fuel cycle path for over thirty different fuels. It breaks the fuel cycle up into upstream production and distribution of the fuel (well to pump) and downstream vehicle usage (pump to wheel). The GREET model displays energy use and emissions produced from different fuel cycle paths. This report will show the equations used to obtain the values for energy use and emissions as well as the assumptions that were made to insert values into these equations.

The GREET model starts off by analyzing six petroleum-based fuel cycles: petroleum to conventional gasoline (CG), reformulated gasoline (RFG), conventional diesel (CD) (low-sulfur content), reformulated diesel (RFD), liquid petroleum gas (LPG), and electricity via residual oil. The upstream analysis of these fuels goes through three stages: recovery, refining, and distribution. For a given upstream stage, energy input per unit of energy product output is calculated by using the energy efficiency of the stage.

By definition, energy efficiency is the energy output divided by the energy input (including energy in both process fuels and energy feedstock). Thus total energy input is:

$$Energy_{in} = 1/efficiency$$

$Energy_{in}$  = Energy input of a given stage (say, in Btu per Btu of energy product output from the stage)

$Efficiency$  = Energy efficiency for the given stage (defined as [energy output]/[energy input] for the stage).

All of the assumed efficiencies are listed on the INPUT page of the GREET model.

These efficiency values come from previous studies and research at Argonne National Laboratory. The table below shows the efficiencies used for petroleum fuel cycle stages.

Petroleum-Based Fuel-Cycle Stage	GREET	NREL et al. 1991	Delucchi 1991	Ecotrafic, AB 1992	Bentley et al. 1992	Acurex 1995
Crude recovery	98.0	99.2	97.5	97.0	NE	NE
Crude T&S	99.5	96.2	99.8	99.3	96.0	NE
CG refining	85.0	NE	NE	84.5	90.0	NE
CG T&S&D	98.5	NE	NE	NE	NE	NE
FRFG2 HC refining <sup>a</sup>	86.0	90.0	81.7	NE	NE	NE
CARFG2 HC refining <sup>a</sup>	85.0	NE	NE	NE	NE	82.8
RFG T&S&D	98.5	97.7	99.2	98.6	98.0	NE
LPG refining	93.5 <sup>b</sup>	NE <sup>c</sup>	94.6	90.0	NE	93.2
LPG T&S&D	97.9 <sup>d</sup>	NE	99.0	97.5	NE	NE
Residual refining	95.0 <sup>b</sup>	NE	94.9	97.0	NE	NE
Residual T&S&D	99.0 <sup>d</sup>	NE	99.0	NE	NE	NE
CD refining	89.0 <sup>b</sup>	NE	93.0	NE	NE	NE
CD T&S&D	98.6 <sup>d</sup>	NE	99.1	NE	NE	NE
RFD refining	87.0	NE	NE	NE	NE	NE
RFD T&S&D	98.6 <sup>d</sup>	NE	NE	NE	NE	NE

<sup>a</sup> In order to meet the oxygen requirements of RFG, oxygenates such as methyl tertiary butyl ether (MTBE), ethyl tertiary butyl ether (ETBE), tertiary amyl methyl ether (TAME), or ethanol can be blended into gasoline. Refining efficiencies listed here for RFG HC are for production of the hydrocarbon portion of the RFG in refineries. Energy use and emissions of oxygenate production are calculated separately in GREET. Oxygenates have high octane numbers. Because of the so-called octane enhancement effect by oxygenates, some researchers expect that production of the HC portion of RFG may not be subject to an energy efficiency penalty relative to CG production. The efficiency assumptions here reflect that expectation.

<sup>b</sup> On the basis of the refining intensity involved in generating each product, the GREET model assumes that the order of refinery efficiency (from low to high) is RFG, CG, RFD, CD, LPG, and residual oil.

<sup>c</sup> NE = not estimated.

<sup>d</sup> Primarily on the basis of the energy content per gallon of each fuel, the GREET model assumes that the order of T&S&D efficiency (from low to high) is LPG, RFG, CG, RFD, CD, and residual oil. Besides the energy content of each fuel, transportation distance and length of storage time affect the T&S&D efficiency of each product. While efficiency values for CG and residual oil are simply assumed, the efficiency values for LPG, RFG, CD, and RFD are calculated by using the efficiency of CG and the energy content of LPG, RFG, CD, and RFD.

Figure 3.1: Energy efficiencies of petroleum based fuel cycle stages (%)

Upstage emissions of VOCs, CO, NO<sub>x</sub>, PM<sub>10</sub>, SO<sub>x</sub>, CH<sub>4</sub>, N<sub>2</sub>O, and CO<sub>2</sub> for a particular stage are calculated in grams per million Btu of fuel throughput from the stage. Emissions from combustion of process fuels for a particular stage are calculated by using the following formula:

$$EM_{cm,i} = (\sum_j \sum_k EF_{i,j,k} * EC_{j,k}) / 1,000,000$$

$EM_{cm,i}$  = Combustion emissions of pollutant i in g/10<sup>6</sup> Btu of fuel throughput

$EF_{i,j,k}$  = Emission factor of pollutant i for process fuel j with combustion technology k (g/10<sup>6</sup> Btu of fuel burned)

$EC_{j,k}$  = Consumption of process fuel j with combustion technology k (Btu/10<sup>6</sup> Btu of fuel throughput)

$EC_{j,k} = EC * Share_{fuelj} * Share_{techk,j}$

$EC$  = Total energy consumption for the given stage (in Btu/10<sup>6</sup> Btu of fuel throughput)

$Share_{fuelj}$  = Share of process fuel j out of all process fuels consumed during the stage  $\sum_j fuel_j = 1$

$Share_{techk,j}$  = Share of combustion technology k out of all combustion technologies for fuel j ( $\sum_k tech_{k,j} = 1$ )

Combustion technology shares ( $Share_{techk,j}$ ) for a given process fuel are influenced by technology performance, technology costs, and emission regulations for stationary sources. In GREET, default technology shares are assumed for each upstream stage. In most cases, for a given combustion technology, GREET has two sets of emission factors: current and future. Emission factors of combustion technologies by fuel type are presented on the EF page of GREET 1.5a. Emission factors ( $EF_{i,j,k}$ ) for , CO, NO<sub>x</sub>, PM<sub>10</sub>, CH<sub>4</sub>, and N<sub>2</sub>O for different combustion technologies fueled by different process fuels are primarily derived from the fifth edition of EPA's AP-42 document (EPA 1995).

In the GREET model, SO<sub>x</sub> emission factors for combustion technologies fueled with all fuels except coal, crude oil, and residual oil are calculated by assuming that all sulfur contained in these process fuels is converted into sulfur dioxide (SO<sub>2</sub>). The following formula is used to calculate the SO<sub>x</sub> emissions of combustion technologies:

$$SO_{xj} = Density_j \div LHV_j \times 1,000,000 \times S\_ratio_j \times 64 \div 32$$

$SO_{xj}$  = SO<sub>x</sub> (primarily SO<sub>2</sub>) emission factor for combustion of process fuel j (in g/10<sup>6</sup> Btu of fuel j burned);

$Density_j$  = Density of process fuel j (in grams per gallon [g/gal] for liquid fuels, grams per standard cubic foot [g/scf] for gaseous fuels, or grams per ton [g/ton] for solid fuels)

$LHV_j$  = Low heating value of process fuel j (in Btu/gal for liquid fuels, Btu/scf for gaseous fuels, and Btu/ton for solid fuels)

$S\_ratio_j$  = Sulfur ratio by weight for process fuel j

64 = Molecular weight of SO<sub>2</sub>

32 = Molecular weight of elemental sulfur

Uncontrolled SO<sub>x</sub> emission factors associated with combustion of residual oil, crude oil, and coal are very high. For these cases, SO<sub>x</sub> emission factors for various combustion technologies are derived from the fifth edition of EPA's AP-42 document.

In GREET combustion CO<sub>2</sub> emission factors in g/10<sup>6</sup> Btu of fuel throughput are calculated by using a carbon balance approach. Through the approach, the carbon contained in a process fuel burned minus the carbon contained in combustion emissions of VOCs, CO, and CH<sub>4</sub> is assumed to convert to CO<sub>2</sub>. The following formula is used to calculate CO<sub>2</sub> emissions:

$$CO_{2,j,k} = [Density_j \div LHV_j \times 1,000,000 \times C\_ratio_j - (VOC_{j,k} \times 0.85 + CO_{j,k} \times 0.43 + CH_{4,j,k} \times 0.75)] \times 44 \div 12$$

$CO_{2,j,k}$  = Combustion CO<sub>2</sub> emission factor for combustion technology k burning process fuel j (in g/10<sup>6</sup> Btu of fuel j burned)

$Density_j$  = Density of process fuel j (in g/gal for liquid fuels, g/scf for gaseous fuels, or g/ton for solid fuels)

$LHV_j$  = Low heating value of process fuel j (in Btu/gal for liquid fuels, Btu/scf for gaseous fuels, and Btu/ton for solid fuels)

$C\_ratio_j$  = Carbon ratio by weight for process fuel j

$VOC_{j,k}$  = VOC emission factor for combustion technology k burning process fuel j (in g/10<sup>6</sup> Btu of fuel j burned)

0.85 = Estimated average carbon ratio by weight for VOC combustion emissions

$CO_{j,k}$  = CO emission factor for combustion technology k burning process fuel j (in g/10<sup>6</sup> Btu of fuel j burned)

0.43 = Carbon ratio by weight for CO

$CH_{4,j,k}$  = CH<sub>4</sub> emission factor for combustion technology k burning process fuel j (in g/10<sup>6</sup> Btu of fuel j burned)

0.75 = Carbon ratio for CH<sub>4</sub>

44 = Molecular weight of CO<sub>2</sub>

12 = Molecular weight of elemental carbon

The above formula shows the calculation method for combustion CO<sub>2</sub> emissions by which carbon contained in VOC, CO and CH<sub>4</sub> is subtracted. On the other hand, VOCs and CO reside in the atmosphere for less than 10 days before they decay into CO<sub>2</sub>. In GREET 1.5, the indirect CO<sub>2</sub> emissions from VOCs and CO decay in the atmosphere are considered.

### ***3.2 Biodiesel Calculations in GREET***

The GREET model does an excellent job of estimating the energy use and emissions that result from the soybean to biodiesel fuel cycle. The model is very complete, analyzing the inputs and outputs for each step of the process. This section is a breakdown of the default biodiesel calculations in GREET.

First the GREET makes assumptions for the amount of soybeans yielded per unit area, the oil content of these soybeans, and their uses. This data was obtained from actual statistics presented by the Food and Agricultural Policy Research Institute, and the results are shown in table 3.1 below.

<b>Parameter</b>	<b>1996<sup>a</sup></b>	<b>1997<sup>b</sup></b>	<b>2000<sup>b</sup></b>	<b>2005<sup>b</sup></b>
Amount planted (10 <sup>6</sup> acres)	62.6	64.2	63.7	63.3
Amount harvested (10 <sup>6</sup> acres)	61.6	63.4	62.7	62.3
Yield (bu/acre harvested)	35.3	37.6	39.4	42.2
Production (10 <sup>6</sup> bu)	2,177	2,382	2,473	2,632
Domestic use (10 <sup>6</sup> bu) <sup>c</sup>	1,481	1,514	1,582	1,709
Exports (10 <sup>6</sup> bu) <sup>c</sup>	851	895	883	926
Soybean meal production (10 <sup>3</sup> tons)	32,513	33,137	34,996	37,936
Domestic meal use (10 <sup>3</sup> tons)	26,581	26,781	28,810	31,381
Meal exports (10 <sup>3</sup> tons)	6,002	6,464	6,274	6,636
Soybean oil production (10 <sup>6</sup> lb)	15,236	15,270	16,434	17,854
Domestic soybean oil use (10 <sup>6</sup> lb)	13,460	13,661	14,537	15,306
Soybean oil exports (10 <sup>6</sup> lb)	992	1,717	1,900	2,574

**Table 3.1: U.S. Soybean production and deposition**

Next the GREET model analyzes soybean farming, and assumes an energy consumption of 32,104 Btu/bushel. Table 3.2 below shows the usage intensity of fertilizer, energy, and pesticides for soybean farming. The values shown in table 3.2 come from a study done by John Sheehan at the NREL in 1998.

Parameter	Value (1990) <sup>a</sup>	REET Value (2005)
Fertilizer use (g/bu)		
Nitrogen (N)	132.1	119
Phosphate (P <sub>2</sub> O <sub>5</sub> )	414.2	373
Potash (K <sub>2</sub> O)	705.0	635
Herbicide use (g/bu)	53.1	47.8
Insecticide use (g/bu)	0.534	0.48
Energy use share in Btu/bu (%)		
Gasoline	10,570 (29.6)	(29.6)
Diesel	23,605 (66.1)	(66.1)
LPG	928 (2.6)	(2.6)
Natural gas	2 (0)	(0)
Electricity	571 (1.6)	(1.6)
Total	35,710 (100)	32,140

**Table 3.2: Usage intensity of fertilizer, energy, and pesticide for soybean farming**

This study analyzed the fertilizer, energy, and pesticides for soybean farming in the 14 main soybean producing states. Because these values are for 1990 they were reduced by 10% to the approximate values for 2005 used in REET.

The soybean oil extraction process is analyzed next. At soybean oil extraction plants, soybeans are crushed and then organic solvents are used to extract the oil. The solvent extraction process is a widely used and well established technology. The standard solvent is n-hexane produced from petroleum, and most of this is recovered and recycled through the process several times. In calculating emissions and energy use n-hexane is assumed to be produced from crude, and its upstream production energy use



and emissions are adopted from energy use and emissions calculated for producing liquid petroleum gas. Steam is also used in the oil extraction process and is assumed to be generated from natural gas. The inputs and outputs of the soybean oil extraction process are shown in table 3.3 below.

Inputs and Outputs	Ahmed et al. 1994 <sup>a</sup>		Sheehan et al. 1998	GREET Values <sup>b</sup>
	Current Average	Industry Best		
Input				
Soybean (lb)	5.49	5.49	5.89	5.70
Steam (Btu) <sup>c</sup>	3,151	1,716	2,919	2,900 (44.5%)
NG (Btu)	0	0	2,826	2,800 (43.0%)
Electricity (kWh)	0.089	0.074	0.186	0.18 (9.4%)
N-hexane (Btu)	205	64	206	205 (3.1%)
Total energy (Btu)	3,660	2,032	6,586	6,519 (100%)
Output				
Soy oil (lb)	1	1	1	1
Soy meal (lb)	4.32	4.32	4.48	4.48

**Table 3.3: Inputs and outputs of soybean oil extraction plants**

Next the transesterification process is modeled. This data again comes from studies done by John Sheehan and Ahmed from the National Soy Diesel Development Board. Table 3.4 shows the results from the transesterification process.

Inputs and Outputs	Ahmed et al. 1994			GREET Default Value
	Industry Average	Industry Potential	Sheehan et al. 1998	
Inputs				
Soy oil (lb)	1.04	1.04	1.04	1.04
Steam (Btu)	2,470	507	1,864	1,865
Electricity (kWh)	0.25	0.20	0.013	0.10
Methanol (Btu)	992	1,172	773	800
Sodium hydroxide (Btu)	36.3	45.4	263	263
Sodium methoxide (Btu)	NE <sup>a</sup>	NE	10	10
Hydrochloric acid (Btu)			32	32
Total process energy (Btu) <sup>b</sup>	5,217	3,489	2,802	3,311
Outputs				
Biodiesel (lb)	1	1	1	1
Glycerine (lb)	0.109	0.109	0.213	0.213

**Table 3.4: Inputs and outputs of biodiesel plants with the transesterification process**

The GREET model also considers the energy and emissions that result from transporting the various materials through each step in the process. Each of these processes are then combined resulting in the energy use and emissions produced by the soybean to biodiesel fuel cycle.

## Chapter 4

# Methodology of the Algae Pond Model

### 4.1 NREL Outdoor Test Facility Results

The algae model is based off of the results obtained by NREL at the Outdoor Test Facility (OTF) ponds in Roswell, New Mexico. A description of the facility as well an explanation of why NREL chose this area is given in chapter 2. This site was in operation for three years and the results from the OTF facility are given in table 4.1 below. These results where used extensively in modeling algae farm operations.

Pond Liner	CO <sub>2</sub> use (m <sup>3</sup> /d)	Dates	Productivity (gm afdw/m <sup>2</sup> /d)	Carbon Use Efficiency	Water Loss (mm/d)
YES	15.2	10/1/88 - 9/30/89	9.8	59	5.7
NO	13.4	10/1/88 - 9/30/89	8.3	50	6.2
NO	14.6	10/1/89 - 9/30/90	10.5	82	
YES	22.0	6/1/90 - 10/30/90	19	81	
NO	19.2	5/1/90 - 9/30/90	18	88	

**Table 4.1: Long Term OTF Results from 1,000 square meter Raceways**

Notes: gm/afdw/m<sup>2</sup>/d: grams of ash-free dry mass per square meter per day

Pond liner: YES indicates a plastic lined pond; NO indicated dirt bottom

## 4.2 APM Inputs

### 4.2.1 Solar Radiation

To model the amount of UV radiation that an algae pond receives solar radiation data was obtained from the National Renewable Energy Laboratory (NREL) Resource Assessment Program ([http://rredc.nrel.gov/solar/old\\_data/nsrdb/redbook/atlas/](http://rredc.nrel.gov/solar/old_data/nsrdb/redbook/atlas/)). This site provides maps that display the average solar radiation that an area receives per month. Figure 4.1 is the solar radiation map for the United States for the month of July; the green dot is the location of Roswell, New Mexico.

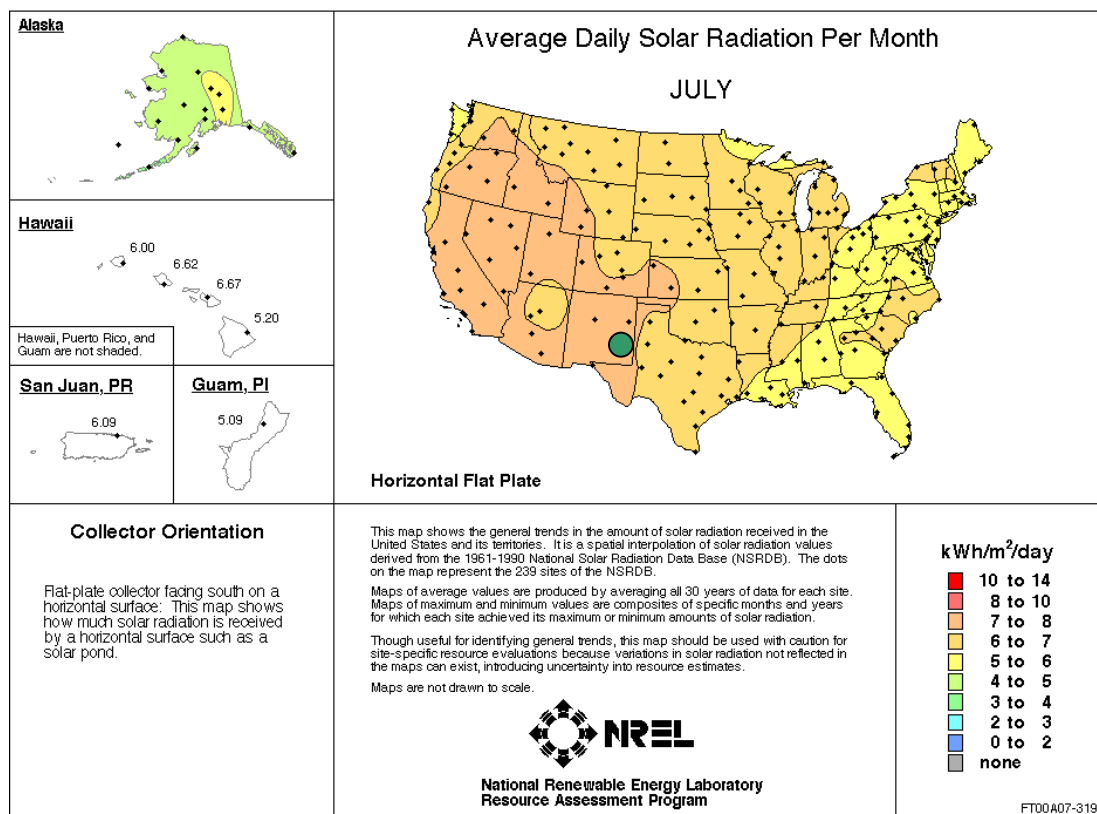


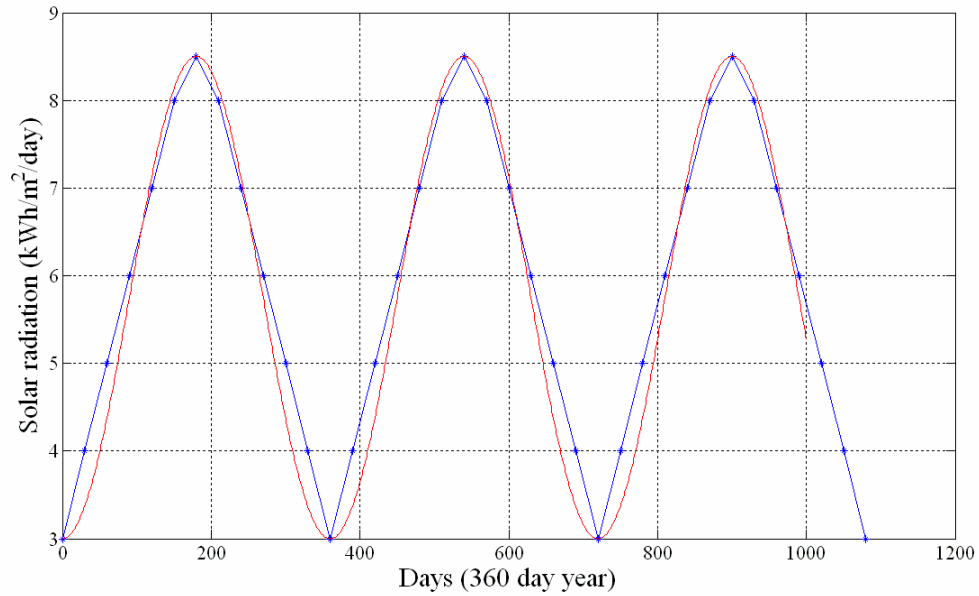
Figure 4.1 – Average solar radiation in the U.S. for the month of July

The solar radiation for each month of the year was determined and can be seen in table 4.2 below.

Month	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Average
kWh/m <sup>2</sup> /d	4	5	6	7	8	8.5	8	7	6	5	4	3	5.9167

**Table 4.2: Average Monthly Solar Radiation in Roswell, New Mexico**

This solar radiation data was plotted against time and a sine wave was fit to the data as shown in the figure below.



**Figure 4.2: Solar Radiation Curve Fit for Roswell, New Mexico**

The corresponding equation for solar radiation in Roswell NM is

$$UV = 2.75 \times \sin(\pi / 180 \times \text{days} - \pi / 2) + 5.75$$

$$UV = \text{Solar radiation (kWh/m}^2\text{/day)}$$

$$\text{days} = \text{number of days (360 days make up one year in simulation)}$$

A sine wave describing the amount of solar radiation that an area receives can be generated using the maximum and minimum values of solar radiation. In the United States the maximum radiation is in June and the minimum is in December. Given these two inputs the solar radiation curve can be determined by the following formula:

$$UV = A \times \cos(\pi / 180 \times days) + avgUV$$

$UV$  = Solar radiation (kWh/m<sup>2</sup>/day)

$days$  = number of days (360 days make up one year in simulation)

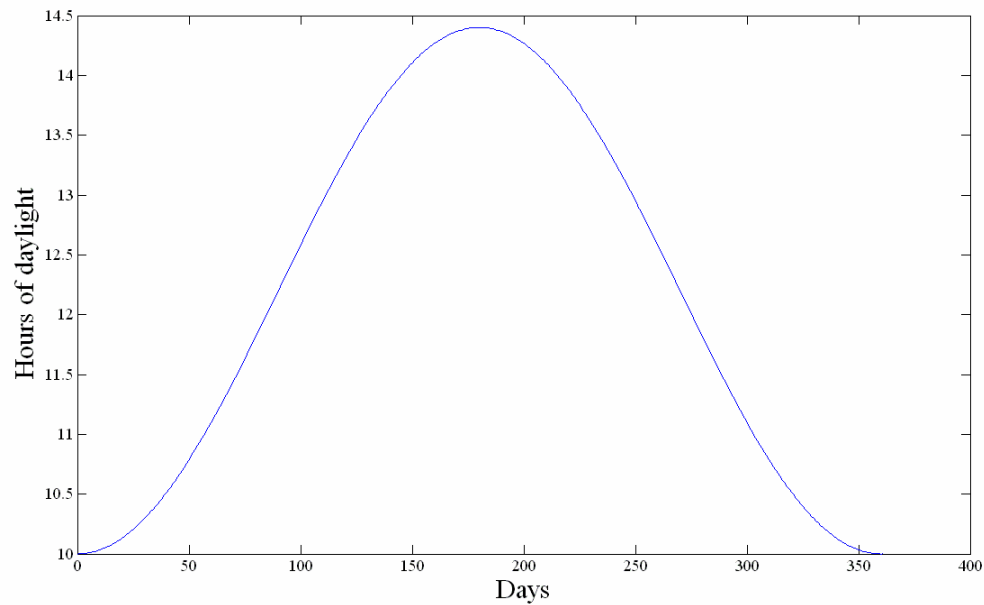
$A$  = (max – min)/2 or (UV\_Jun – UV\_Dec)/2

$avgUV$  = (max + min)/2 or (UV\_Jun + UV\_Dec)/2

#### **4.2.2 Day Length**

The next step in the modeling process is to generate a function of average hours of daylight for a given area for each day of the year. This is vital information because the algae pond should only be operated during daylight hours, because without sunlight the algae do not grow and therefore the operation of the paddle wheel and pumps is a waste of energy.

The model prompts the user to input the average hours of daylight the area receives on December 21 and June 22 the shortest and longest days of the year. The generation of the day light function is done using these values and creating a cosine wave, the same procedure as generating the solar radiation function. The figure below shows the hours of daylight received each day in Roswell New Mexico.



**Figure 4.3: Average day length for Roswell New Mexico**

### ***4.3 Algae Growth***

The micro algae are grown in 1,000 m<sup>2</sup> ponds, which are circulated by a paddle wheel as described in Chapter 2. When grown in this manner the algae are in the light limiting linear growth phase described by the equation

$$IA = u * X * V / Y$$

I = Photon flux density (h J m<sup>-2</sup>)<sup>-1</sup>

A = Illuminated surface area (m<sup>2</sup>)

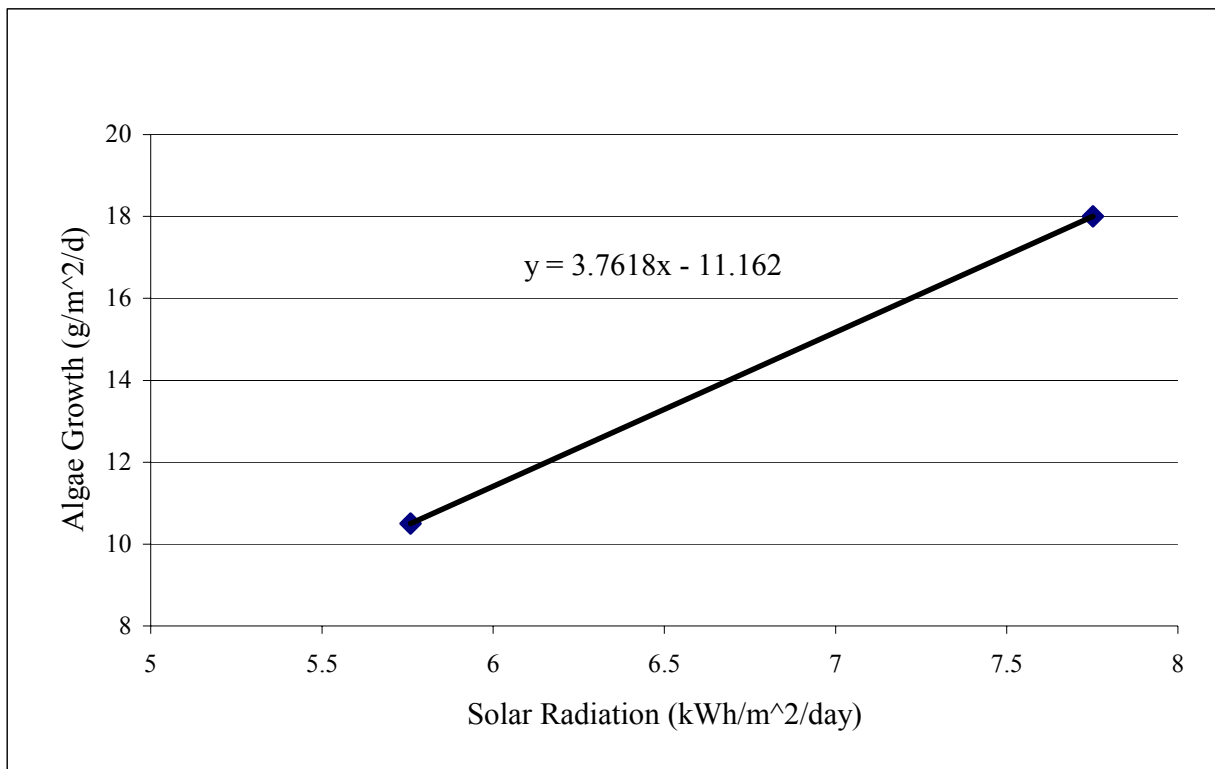
u = Specific growth rate (1 h<sup>-1</sup>)

X = Biomass concentration (grams/liter)

V = Culture volume (m<sup>3</sup>)

Y = Growth yield (g/J)

The major factor effecting algae growth is solar radiation, therefore the modeling of algae growth is based on a calibration between solar radiation and algae growth. The results for algae growth from the OTF operations were calibrated against the amount of solar radiation the area received during that time period to obtain a formula for algae growth based on the amount of solar radiation the pond receives. Figure 4.4 below shows the calibration plot and the corresponding equation relating solar radiation to algae growth. In the equation y is algae growth ( $\text{g/m}^2/\text{d}$ ) and x is solar radiation ( $\text{kWh/m}^2/\text{d}$ ).



**Figure 4.4: Calibration of Algae Growth to Solar Radiation for Roswell NM**



## 4.4 CO<sub>2</sub> Sequestration

The amount of CO<sub>2</sub> sequestered by the algae is a vital part of the algae to biodiesel process. It is the main feedstock for the algae, providing a reduction in the amount of CO<sub>2</sub> injected into the atmosphere from the coal fired electric plants. The amount of CO<sub>2</sub> consumed was determined from the experimental results achieved in the OTF shown in table 4.1 above. The measured CO<sub>2</sub> consumption was calibrated against the recorded algae growth rate as shown in figure 4.5 below.

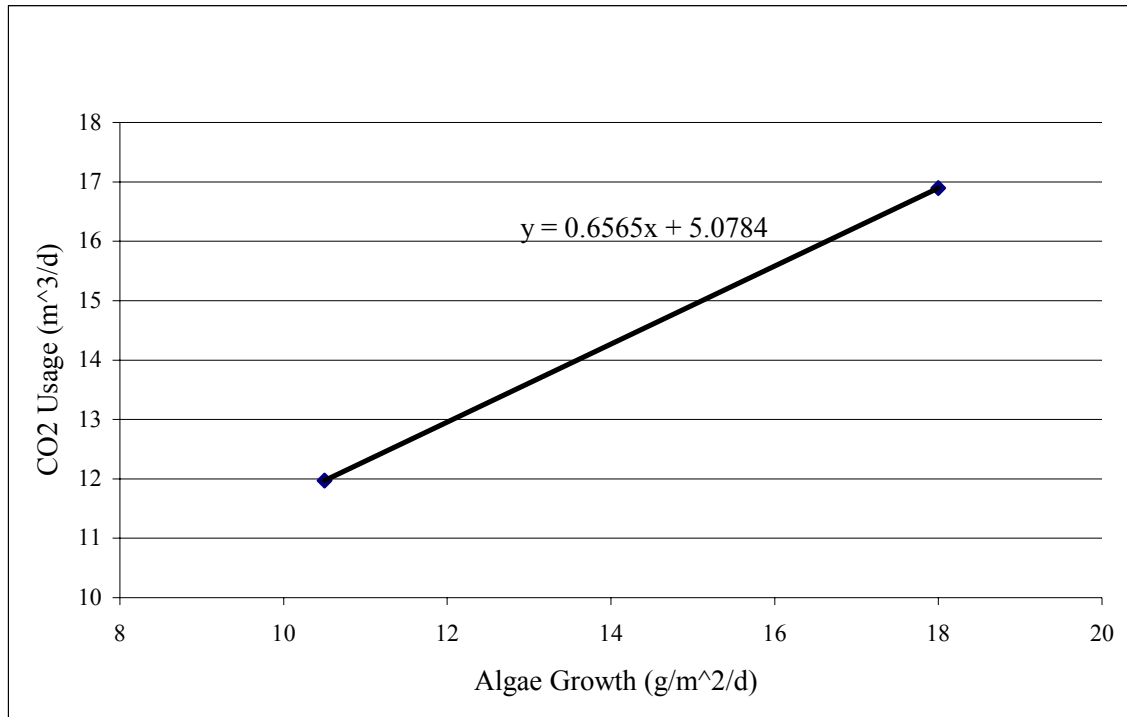


Figure 4.5: Calibration of CO<sub>2</sub> Usage and Algae Growth

A straight line curve fit resulted in the following equation:

$$CO_2consumed = 0.6565 \times AlgaeGrowth + 5.0784$$

$CO_2consumed$  = Amount of CO<sub>2</sub> consumed by the pond per day (cubic meters)

$AlgaeGrowth$  = Amount of new algae growth per day (g)

However because this process is only 80% efficient the equation must be modified in order to ensure that the algae receive the required amount of CO<sub>2</sub> to achieve maximum growth. The equation used in the Algae Pond Model is:

$$CO_2consumed = (0.6565 \times AlgaeGrowth + 5.0784) / 0.8$$

#### ***4.5 Fertilizer Consumption***

There are two elements that must be used to fertilize the algae, they are nitrogen and phosphorous. Nitrogen can be added to the ponds in the form of ammonia or nitrate, and should be mixed at 0.8% of the dry weight of the algae in the pond. Phosphorous as phosphate should be mixed at 0.6% of the dry weight (Benemann, 2006). The percentage of each element required by the algae ponds was given to me by Dr. John Benemann, who was one of the lead scientists on the Aquatic Species Program and has extensive experience and expertise in the field. The Algae Pond Model multiplies these percentage by the amount of daily growth, to determine the amount of Nitrogen and Phosphorous required by the pond.

#### ***4.6 Water Consumption***

The OTF ponds recorded an average water loss of 6.2 mm or 6.2 cubic meters of water per day due to evaporation. Although this is not a constant daily value in reality, the Algae Pond Model will assume a daily water loss of 6.2 cubic meters. The evaporation rate is a function of solar radiation, temperature, wind velocity over the pond

surface, and current velocity of the pond. These are variables that should be considered by the Algae Pond Model in the future in order to properly model the amount of water required by the ponds.

## ***4.7 Electricity Use***

### ***4.7.1 Paddle Wheel***

Electricity is the major energy source used to power algae farm operations. The amount of power required for paddle wheel, pumping and centrifuge operations were determined from previous studies and current equipment specs, and are given in table 4.3 below.

Operation	Average Daily Power Consumption (kWh)	Average Yearly Power Consumption (kWh)	Percentage of Algae Farm Operations
Paddle Wheel	1.23	441.2	17%
Pumping	2.01	722.7	27%
Centrifuge	4.11	1480.6	56%
<b>Total</b>	<b>7.35</b>	<b>2644.5</b>	

**Table 4.3: Electricity Consumption of 1,000 m<sup>2</sup> algae pond**

The amount of power required by the paddle wheel was determined during OTF operations to be 0.1 kW (Benemann, 1996). This value is then multiplied by the number of hours of operation per day giving a certain number of kilowatt hours of electricity used per day. The hours of operation correspond to the hours of daylight because as long as there is solar radiation the algae are growing and the pond must be in operation.

#### 4.7.2 Pumping

Water will be pumped to and from the ponds using a Marlow Pumps Self-priming Centrifugal Pump model: 4B-PEL. This pump was selected because it is capable of effectively pumping water containing algae up to 5% by volume. This pump is rated to move 550 gal/min of algae sludge up to 15 feet vertical displacement at 15 horsepower, or one kilowatt hour will pump 11.4 cubic meters of algae water. To determine how much power is required to operate the pond, the amount of water to be pumped must be known.

The amount of water to be pumped will be the amount of water pumped from the raceway pond to the settling pond, plus the amount of recycled water pumped from the settling pond back to the raceway pond, and the amount of fresh water that must be pumped due to evaporation. The amount of water pumped into the settling pond is a function of algae growth rate corresponding to the equation:

$$\text{SettlingPond} = \%Pond \times \text{AlgaeGrowth}$$

$$\text{SettlingPond} = \text{Amount of water pumped from raceway to settling pond (m}^3\text{)}$$

$$\%Pond = \text{Constant equal to (10/10.5) or average amount of raceway pumped per day (5\% by vol. or 10 m}^3\text{) divided by the average growth (kg/day)}$$

$$\text{AlgaeGrowth} = \text{(kg) of daily algae growth}$$

The amount of recycled water pumped from the settling pond back to the raceways is given by the equation:

$$\text{SettlingPond}_{\_recycled} = \text{SettlingPond} \times \%SettlingPond$$

$$\text{SettlingPond}_{\_recycled} = \text{Water pumped from settling pond to raceway (m}^3\text{)}$$

$$\%SettlingPond = \text{Constant equal to 67\% or volume of settling pond recycled}$$

These two values are combined with the amount of water that results from evaporation resulting in the total volume of water being pumped per day as shown in the equation:

$$TotalDailyPumping = SettlingPond\_recycled + SettlingPond + evaporation$$

$$TotalDailyPumping = (m^3) \text{ Amount of water pumped per day}$$

The amount of power required to for pumping is then determined by dividing the amount of water pumped per day by the rated power of the Marlow Pump model 4B-PEL.

$$DailyPumpingPower = TotalDailyPumping / Pump\_power$$

$$DailyPumpingPower = (kWh) \text{ Amount of power required to operate pumps}$$

$$Pump\_power = \text{Constant } (11.4 \text{ m}^3 / 1 \text{ kWh}) \text{ from pump specs}$$

#### 4.7.3 Centrifuge

The Algae Pond Model's centrifuge calculations are based on the operation of the Alfa Laval CH-36B GOF Separator Nozzle centrifuge, a picture of this device along with its technical specifications is shown in figure 4.6 below.



#### ALFA LAVAL CH-36B GOF Separator Nozzle Centrifuge

##### Technical specifications

Max. throughput capacity	225 m3/h
Max. nozzle flow	160 m3/h
Max. rotation	2900 rpm
Max. G-force	4300 G
Feed temperature range	0-100 °C
Installed motor power	190/225 kW
Noise level (ISO 3744 or 3746)	85 dB

**Figure 4.6: Picture and Technical Specifications of the Alfa Laval CH-36B nozzle type centrifuge used in the Algae Pond Model**

This centrifuge was recommended by Dr. Nick Nagle with the NREL, who worked on the Aquatic Species Program and has had extensive experience with the mass culture and harvesting of microalgae (Personal communication).

The amount of power consumed by the centrifuge is found using the equation:

$$\text{CentrifugePower} = \text{SettlingPond} \times 33\% \div \text{CentThru} \times \text{CentPower}$$

*CentrifugePower* = (kWh) Amount of power required by centrifuge  
corresponding to daily algae growth

*SettlingPond* = Amount of water pumped from raceway to settling pond (m<sup>3</sup>)

33% = Amount of mixture from settling pond that goes thru the centrifuge

*CentThru* = Constant 180 (m<sup>3</sup>/hr)

*CentPower* = Constant 225 (kW)

The amount of algae water put through the centrifuge was determined to be 180 m<sup>3</sup>/hr which is 80% of the rated max throughput capacity. The centrifuge cannot operate at the maximum throughput capacity, because the algae water entering the centrifuge is 3% algae and the particles are very small in size (Alga Laval spec sheet). The power consumption of the various algae pond operations are summed resulting in the energy or electricity usage for the pond, this value is plotted so the user can see the amount of daily electricity required for pond operations.

## ***4.8 Transfer to GREET Model***

### ***4.8.1 Model Separation***

The outputs of the Algae Pond Model (APM) need to be inserted into the GREET model along with a few modifications in order to analyze the energy use and emissions of

the entire fuel cycle. The APM models the algae farm operations up to harvesting and storage of dry algae mass. The dry algae mass then goes through the oil extraction process, which is a batch process very similar to the soybean oil extraction process. It was determined that the soybean oil extraction model in GREET can be used to model algae oil extraction (Personal conversation Nagle). Therefore the GREET model is used to analyze the algae to biodiesel fuel cycle from oil extraction to vehicle use. Figure 4.7 below shows a schematic of the algae to biodiesel process, depicting which steps of the process are modeled using the APM and which are modeled in GREET.

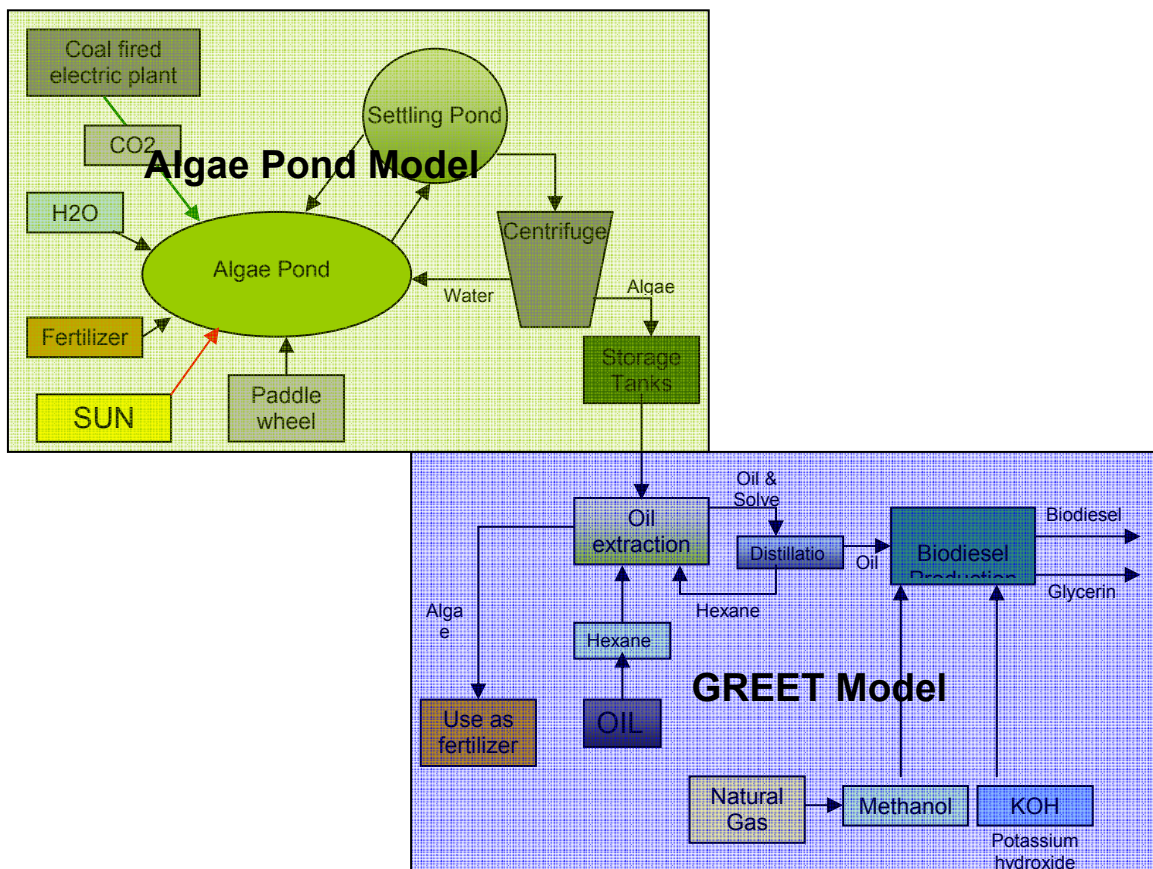


Figure 4.7: Schematic of Algae to Biodiesel Fuel Cycle depicting which steps are modeled using the APM and which are modeled using GREET

#### ***4.8.2 GREET Model Modifications***

Several need to be made to the default GREET model in order to accurately model the algae to biodiesel process as appose to the soybean to biodiesel process. The GREET model should be run for long term results INPUT sheet cell B3, all of the other changes will be made on the biodiesel BD worksheet in the GREET model. First the shares of process fuels must be adjusted because soybean farming uses diesel fuel, gasoline and electricity whereas algae farm operations only use electricity. Therefore zeros need to be entered into cells B43 B44 and B47, while 100% needs to be entered into cell B48. Next, algae have higher oil content then soybeans, which results in the production of more biodiesel per bushel. The GREET model uses a default value of 5.7 pounds of soybeans to produce 1 pound of oil, however the algae species used in the model requires only 5 pounds of algae to produce 1 pound of oil. Therefore cell C11 must be changed from 5.7 to 5. The amount of fertilizers and pesticides must also be adjusted. Nitrogen used cell C38 must be changed from 107.1 to 217.4 grams/bushel. Phosphorus used cell D38 must be changed from 335.7 to 163.1 grams/bushel. Potassium, herbicide, and pesticide cells E38, F38, and G38 all need to be changed to zero. With these modifications made the GREET model is now ready to accept inputs from the APM and accurately model the algae to biodiesel cycle. Figure 4.8 below lists the changes that need to be made to the GREET model in order to model the algae to biodiesel process.



### ***Algae to biodiesel modifications to default GREET***

All changes made in biodiesel sheet (BD)

Enter zeros in cells B43 B44 and B47

Enter 100% in cell B48

Change C11 from 5.7 to 5

Change C38 from 107.1 to 217.4

Change D38 from 335.7 to 163.1

Enter zeros into cells E38, F38, and G38

**Figure 4.8: Algae to biodiesel modification to default GREET Model**

#### ***4.8.3 Data Transfer from APM to GREET***

The APM outputs the amount of energy (Btu) required to produce one bushel or 60 pounds of ash free dry algae mass in the Matlab command window. This value is determined by dividing the total amount of energy used for the year by the number of bushels produced. The user must enter this value into the GREET model sheet BD cell B38 replacing the default soybean farming input of 28,926 Btu/bushel. Next the APM outputs the amount of CO<sub>2</sub> sequestered or used by the algae pond. This value needs to be subtracted from the GREET value for CO<sub>2</sub> usage. The user must enter the CO<sub>2</sub> emissions cell B79 by clicking on it once, then the amount of CO<sub>2</sub> sequestered in the APM needs to be subtracted from the entire default GREET formula. The input cells that must be changed are highlighted in red in figure 4.8 below. By making this adjustment the GREET model will now determine the energy use and emissions that result from algae pond operations as well as for the entire fuel cycle.

34	<b>3) Calculations of Energy Consumption and Emissions for each stage</b>							
35		<b>Soybeans</b>						So
36		<b>Soybean Farming</b>	<b>Soybean Farming Fertilizer Use (grams/bushel)</b>			<b>Soybean Farming Herbicide and Pesticide Use (grams/bushel)</b>		<b>Soybean Transportation</b>
37		Btu/bushel	Nitrogen	P2O5	K2O	Herbicide	Pesticide	Per bushel
38	<b>Material Inputs</b>	28,926	107.1	335.7	571.5	43.02	0.43	
39	<b>Urban emission share</b>	1.0%						
40	<b>Loss factor</b>							
41	<b>Shares of process fuels</b>							
42	Residual oil	0.0%						
43	Diesel fuel	66.2%						
44	Gasoline	29.6%						
45	Natural gas	0.0%						
46	Coal	0.0%						
47	Liquefied petroleum gas	2.6%						
48	Electricity	1.6%						
49	N-hexane (a solvent from crude)	0.0%						
50	Methanol	0.0%						
51	Sodium hydroxide	0.0%						
52	Sodium methoxide	0.0%						
53	Hydrochloric acid	0.0%						
54	Feed loss	0.0%						
55	<b>Energy consumed. Btu/mmBtu of fuel throughput, except as noted</b>	<b>Per bushel of soybeans</b>						P.
56	Residual oil	0						
57	Diesel fuel	19,149						
58	Gasoline	8,562						
59	Natural gas	0						
60	Coal	0						
61	Liquefied petroleum gas	752						
62	Electricity	463						
63	N-hexane (a solvent from crude)							
64	Methanol							
65	Sodium hydroxide							
66	Sodium methoxide							
67	Hydrochloric acid							
68	Total energy	35,295	5083	5357	4070	11432	130	6,008
69	Fossil fuels	35,034	4941	4871	3727	10934	124	5,990
70	Petroleum	30,703	38	989	878	5525	63	5,502
71	<b>Total emissions. grams/mmBtu of fuel throughput, except as noted</b>	<b>Per bushel of soybeans</b>						P.
72	VOC	3.393	0.023	0.047	0.046	0.082	0.001	0.191
73	CO	15.995	0.204	0.189	0.179	0.442	0.007	0.696
74	NOx	22.782	0.295	0.784	0.805	1.330	0.023	2.933
75	PM10	0.883	0.029	0.061	0.051	0.129	0.001	0.063
76	SOx	2.923	0.161	0.609	0.470	0.985	0.013	0.191
77	CH4	3.463	0.862	0.648	0.510	1.282	0.014	0.528
78	N2O	0.065	0.006	0.007	0.006	0.011	0.000	0.013
79	CO2	2,752	340	447	353	904	10	481
80	VOC loss: evaporation				1.492	NO from nitrogen fertilizer		
81	VOC loss: spillage				2.188	N2O from nitrogen fertilizer		
	<b>Urban emissions:</b>							

Figure 4.9: Default GREET Model biodiesel worksheet with algae to biodiesel modification cells highlighted in yellow and APM input cells highlighted in red

## Chapter 5

# Modeling and Simulation Results

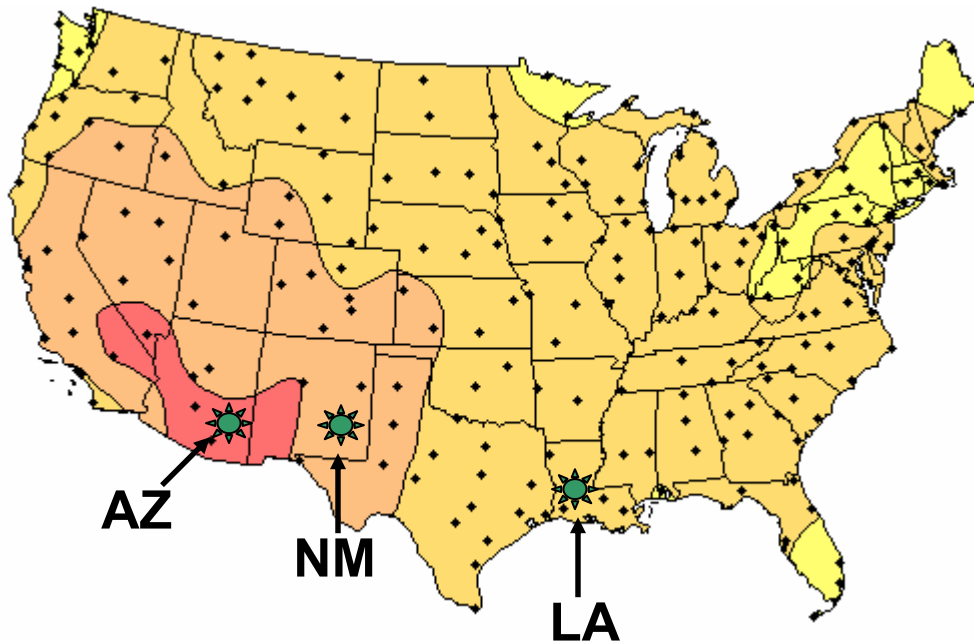
### *5.1 Algae Pond Model Results*

This chapter examines the results from running the Algae Pond Model for three suitable locations for algae operations. These locations were chosen because each of the areas receives large daily amount of solar radiation, and they all have mild winters ensuring year long operation. There is a coal fired electric plant and barren land at each of the sites providing the necessary resources for algae pond operations. Table 5.1 below shows the location, solar radiation, and hours of daylight for the selected sites. This information was input into the APM.

<b>Power Plant Location</b>	<b>Hours of daylight Dec. 21</b>	<b>Hours of daylight Jun. 22</b>	<b>Average UV radiation in Dec.</b>	<b>Average UV radiation in Jun.</b>
Rodemacher Boyce, LA	10.1	14.2	3	7.5
Escalante Roswell, NM	10	14.4	3	8.5
Coronado St. Johns, AZ	10	14.3	3.5	9.5

**Table 5.1: Location and solar radiation data for perspective algae to biodiesel sites**

Figure 5.1 below shows the location of each of the simulation sites. The green stars represent the site locations, the Rodemacher plant in Boyce, LA is given by the abbreviation LA, the Escalante plant in Roswell, NM is given by NM and the Coronado plant is given by the abbreviation AZ.

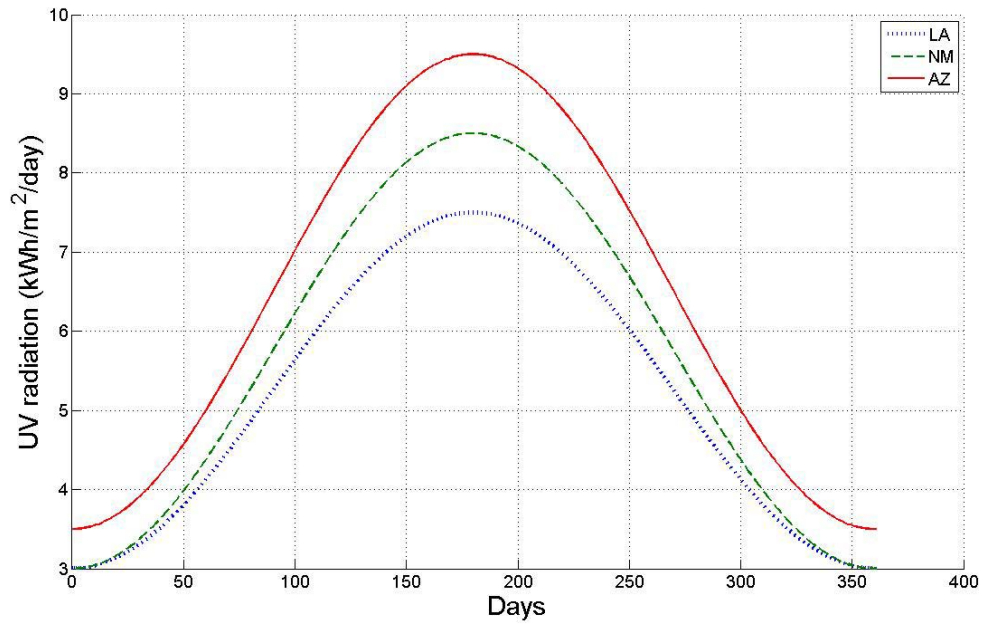


**Figure 5.1: Location of algae simulation sites, the green stars mark location of sites**

After the values from table 5.1 are input into the APM in MatLab, the program cycles through the operations described in Chapter 4 Methodology of Algae Pond Model, and creates the following outputs.

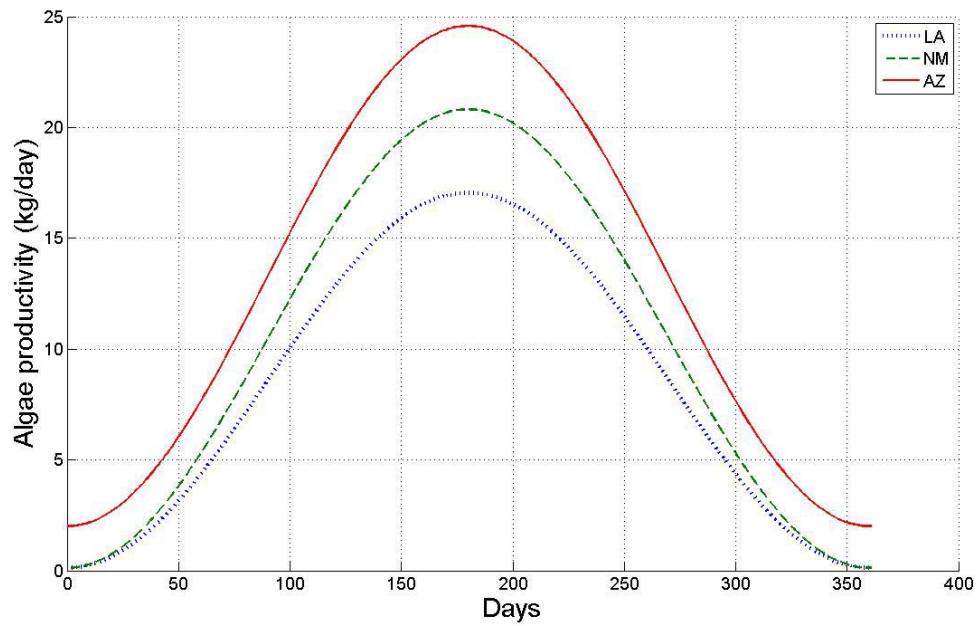
The APM outputs 5 figures, the first is the amount of daily solar radiation that impacts the area for each day of the year beginning on January 1<sup>st</sup>, as shown in figure 5.2 below. It is evident in figure 5.2 that the Coronado site in Arizona receives the most solar radiation per day, this will correlate to faster algae growth, and higher biodiesel

production per unit area then the other sites.



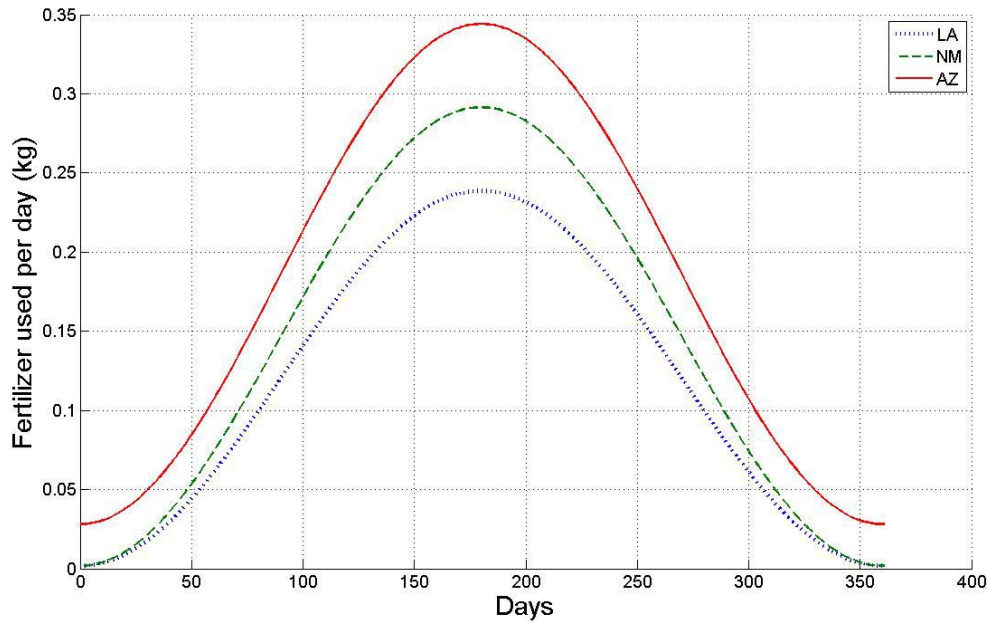
**Figure 5.2: Daily solar radiation**

Next the APM generates a plot showing the daily algae productivity, and as expected the Arizona location (AZ) has the highest daily productivity. Figure 5.3 is the plot of algae productivity per day. The daily productivity will directly impact the amount of fertilizer, CO<sub>2</sub>, and electricity consumed per day.



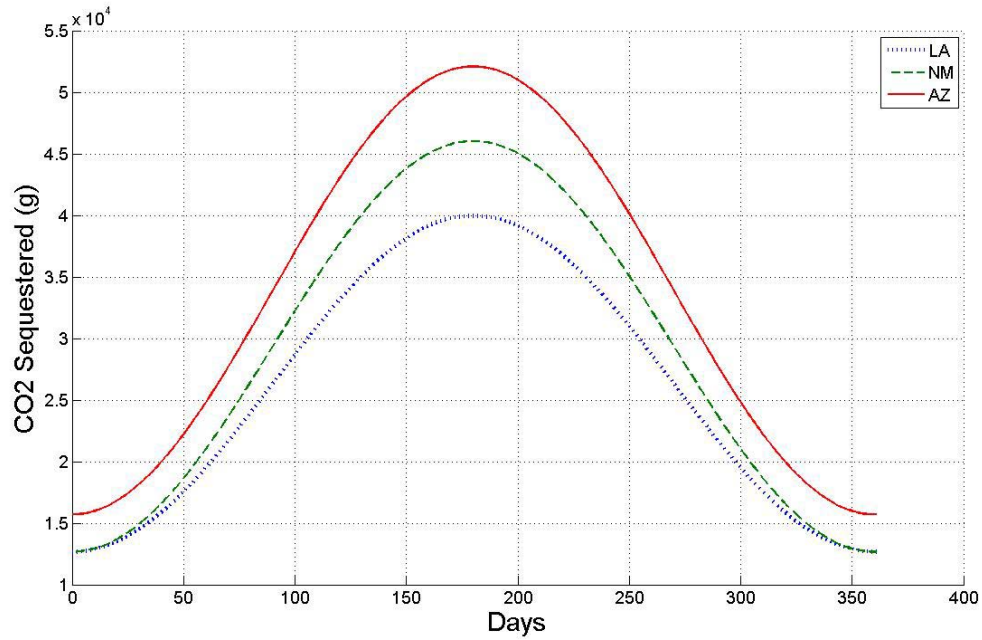
**Figure 5.3: Daily algae productivity**

Figure 5.4 displays a plot showing the fertilizer usage per day at each location. The amount of fertilizer used is directly related to algae growth, because fertilizer like  $\text{CO}_2$  is the feedstock for the algae, and therefore higher algae growth rates result in higher consumption of nutrients, or fertilizer and  $\text{CO}_2$ .



**Figure 5.4: Daily fertilizer usage**

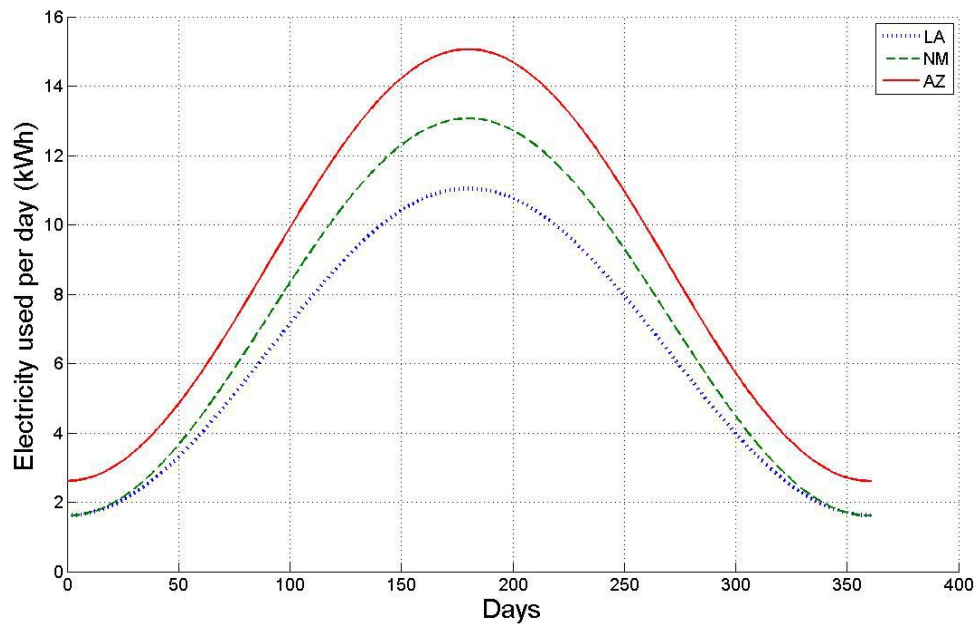
Next the APM outputs the amount of CO<sub>2</sub> sequestered or consumed daily by the algae pond. This is vital when trying to determine the size of operation or the number of algae ponds that can be sustained at a given location. A coal fired electric plant produces a set number of tons of CO<sub>2</sub> daily, this number divided by the maximum amount of CO<sub>2</sub> sequestered by a single pond gives the number of ponds that can be sustained by the coal fired electric plant. Figure 5.5 below shows the amount of CO<sub>2</sub> sequestered daily at the given locations, with the maximum amount sequestered occurring when algae growth is at its maximum around the end of June.



**Figure 5.5: Daily CO<sub>2</sub> consumption**

Figure 5.6 displays the daily electricity requirements of the pond. Again the Arizona location has the highest energy needs because the higher algae growth rates require more algae water to be pumped from the raceway ponds to the settling ponds, and longer centrifuge operation. The maximum daily electricity required is 15 kWh per day for the algae pond in Arizona.





**Figure 5.6: Daily electricity usage**

In the MatLab command window the APM outputs the amount of biodiesel produced annually at each location, the energy required to produce one bushel (60 lbs) of algae, and the amount of CO<sub>2</sub> sequestered per bushel. These values are then input into the GREET model as described in section 4.8.2. Table 5.2 below displays these results for the three simulation locations and for the soybean to biodiesel cycle. It can be seen in Table 5.2 that the Coronado site in St. Johns, AZ produces the most biodiesel annually and also gives the greatest energy benefit for the algae to biodiesel cycle, which means that it produces 10% more energy than is input into the system. Although all of the simulation sites provide an energy benefit they are all substantially lower than the benefit from the soybean to biodiesel cycle. However using soybeans to produce biodiesel yields much less biodiesel per unit area compared to the algae to biodiesel cycle. At the

Arizona location fourteen times the amount of biodiesel is produced per unit area compared to using soybeans in the Midwest.

Location	Gallons of Biodiesel Produced per year	Energy benefit	GREET Inputs	
			Energy required to produce one bushel of algae (Btu/bushel)	CO2 Sequestered (g/bushel)
Rodemacher Boyce, LA	145	6%	68587	83605
Escalante Roswell, NM	177	8%	65195	76466
Coronado St. Johns, AZ	225	10%	61811	69526
Soybeans Midwest	16	35%	28926	0

**Table 5.2: Production Results using Algae Pond Model for Inputs given in Table 5.1 and for the soybean to biodiesel cycle**

## ***5.2 Coronado Power Plant Case Study***

This section will discuss the full fuel cycle analysis of a proposed alga to biodiesel facility in St. Johns, Arizona near the Coronado Power Plant. As shown in section 5.1 a 1,000 m<sup>2</sup> algae pond in St. Johns, Arizona would produce 225 gallons of biodiesel per year. This is by far the highest yield of any of the test cases, and for this reason has been selected to simulate the development of a large scale alga to biodiesel facility at this location.

The Coronado Power Plant produces has a generating capacity of 785 MW of power, and it produces 19,488 tons of CO<sub>2</sub> daily (CleartheAir, 2000). The maximum daily CO<sub>2</sub> consumption per pond is 54,000 grams per day. As shown in Table 5.3 below

the maximum number of algae ponds that can be supported by the Coronado Plant is 327,399, corresponding to a land area requirement of 245 square miles. This data is shown in Table 5.3 below.

Coronado Plant generating capacity (MW)	CO2 released daily Coronado Power Plant (tons)	Max CO2 consumption per 1000 m <sup>2</sup> pond (g/day)	Max number of ponds supported by Coronado Plant	Total land area (mi <sup>2</sup> )	Annual biodiesel production (gal)
785	19,488	54,000	327,399	245	73,664,840

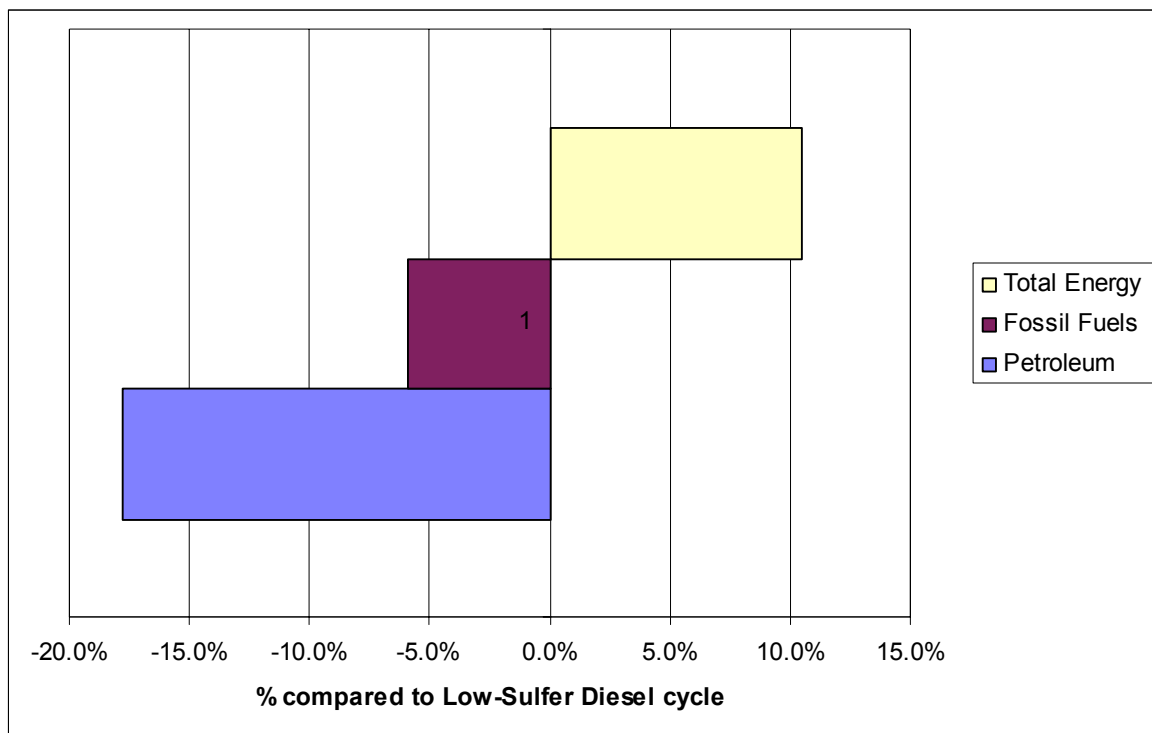
**Table 5.3: Number of ponds and production levels supported by Coronado Power Plant**

To put this into perspective the Coronado Plant produces 0.2 % of the total electricity generated from coal each year according to the United States Energy Information Administration (EIA), and 73 million gallons of biodiesel represents 0.12% of diesel fuel consumption in the United States. Figure 5.7 shows the size and location of the proposed facility.



**Figure 5.7: Size and location of 73 million gallon algae to biodiesel facility near Coronado plant**

Using the GREET model the well to wheel energy use and emissions resulting from producing biodiesel at the Coronado facility were determined. Figure 5.8 is a well to wheel energy use comparison between the biodiesel produced at the Coronado facility and conventional low-sulfur diesel. The biodiesel produced at from the algae is mixed with petroleum diesel to form B20, 20% biodiesel and 80% petroleum diesel. This was chosen because it is an industry standard and the GREET model is setup to analyze B20.

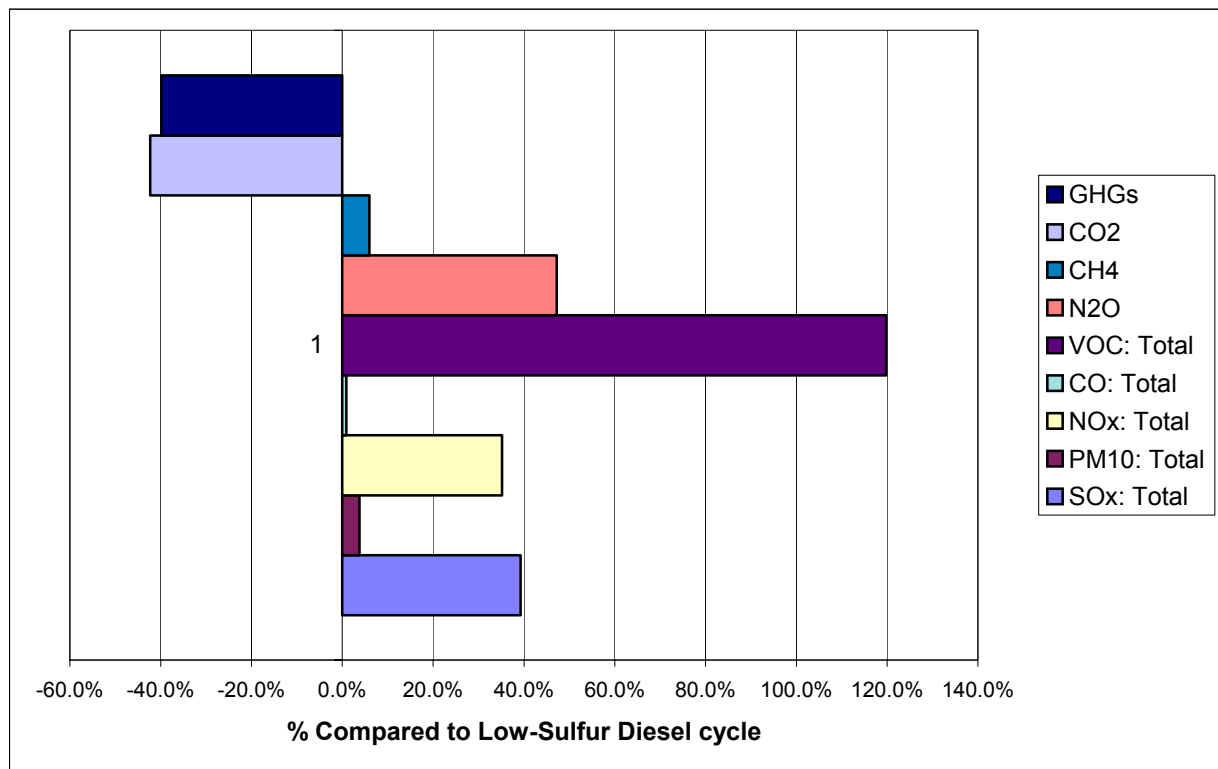


**Figure 5.8: Well to wheel energy use of algae to B20 cycle compared to low sulfur diesel cycle**

It is evident from figure 5.8 that the algae to biodiesel cycle requires about 11% more energy than the low-sulfur diesel cycle. This is because an extensive amount of energy is required for algae farm operations. The conventional diesel cycle requires far less energy upstream because the operation is very simple. The oil is pumped out of the ground, refined, and distributed. However the algae to B20 fuel cycle provides an 18% reduction

in petroleum consumption, which is the number one criterion that an alternative fuel must meet.

The algae to biodiesel fuel cycle provides a substantial reduction in green house gas emissions but increases the emissions of other pollutants. Figure 5.9 is a well to wheel emissions comparison between the biodiesel produced at the Coronado facility and conventional low-sulfur diesel.

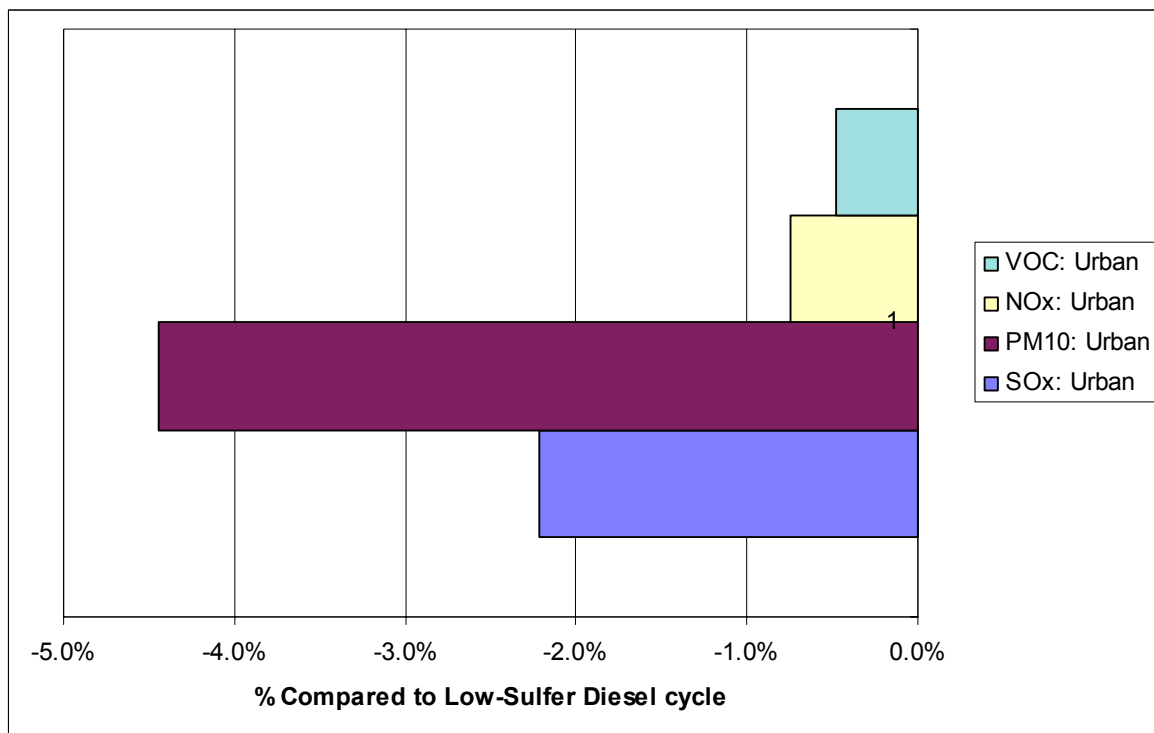


**Figure 5.9: Well to wheel emissions from algae to B20 cycle compared to low sulfur diesel cycle**

The algae to biodiesel fuel cycle provides a 40% reduction in green house gases because the algae sequester large amount of CO<sub>2</sub> in the raceway ponds. However acid rain and smog forming emissions of nitrous oxides NO<sub>x</sub> and sulfur oxides SO<sub>x</sub> are increased by over 30%. This is a result of the coal burned to produce electricity to power the algae

farm operations. These hazardous emissions are emitted at the coal fired electric plants away from cities and the majority of the population.

The algae to biodiesel fuel cycle reduces urban emissions because biodiesel burns cleaner than conventional diesel. Figure 5.10 is a well to wheel urban emissions comparison between the biodiesel produced at the Coronado facility and conventional low-sulfur diesel.



**Figure 5.10: Well to wheel urban emissions from algae to biodiesel fuel cycle compared to low sulfur diesel cycle**

This slight reduction in emissions is a result of using B20 compared to using low-sulfur diesel in conventional vehicles.

## Chapter 6

### Conclusions and Recommendations

#### *6.1 Algae Pond Model (APM) future work*

There are a few modifications that need to be made to the APM in the future so that it provides better results using a more diverse range of inputs. The current version of the APM does not include a temperature input, and therefore can only model locations that do not encounter freezing temperatures. Knowing the temperature at a potential site is required to determine if the algae ponds will freeze during any time of the year. If the ponds freeze the algae will die and production will stop. In the future a temperature function should be built into the APM to more accurately determine production levels, and expand the possible input locations.

The fertilizer consumption modeled by the APM also needs reworked. Currently the amount of fertilizer used is based off of the amount of water being cycled through the ponds. This is not accurate because large amounts of water are lost due to evaporation while the fertilizer remains in the system. A new fertilizer model based on micro algae nutrient consumption needs to be developed.

## ***6.2 Algae biodiesel as an alternative fuel***

It was shown in the introduction of this report that a new energy source, which eliminates the use of petroleum and reduces green house gas emissions must arise if we are to continue our way of life. The use of biodiesel produced from algae was extensively studied and although this fuel cycle does provide substantial reductions in petroleum use and emissions several obstacles must be overcome for algae biodiesel to be an attractive alternative fuel.

First algae harvesting methods must be refined to use less energy. The current methods that involve a centrifuge require too much energy resulting in a 12% increase in total energy required compared to the low-sulfur diesel cycle and only a 10% energy benefit. This also produces very high operating costs making it an unattractive investment.

Second, strains of algae that have higher growth rates and are more resistant to adverse conditions need to be found or created. Although algae produce much higher yields of biodiesel per unit of land compared to any other oil seed crop these production levels can still be dramatically increased. Table 6.1 below shows the amount of biodiesel that is produced per acre at the OTF facility, and although this is almost an order of magnitude higher than the soybean to biodiesel cycle, if laboratory growth rates of 30 g/m<sup>2</sup>/day could be obtained using algae that are 50% oil instead of 20% almost 7000 gallons of biodiesel could be produced annually on an acre of land. If biodiesel could be produced at these staggering production levels this would be a very economically attractive alternative.



Algae	Growth rate (g/m <sup>2</sup> /day)	% Oil of algae by weight	Annual amount of biodiesel produced per acre (gal)
OTF	8.3	20%	700
Laboratory	30	50%	6694

**Table 6.1: Comparison of OTF results to laboratory results**

If these two processes were solved and biodiesel was produced from algae on a large scale, automobile manufactures would need to convert their diesel vehicles to run on B100 or pure biodiesel. If these developments occur biodiesel produced from algae could one day power the transportation network of the future.

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